



(22) Date de dépôt/Filing Date: 2006/01/04

(41) Mise à la disp. pub./Open to Public Insp.: 2007/07/04

(51) Cl.Int./Int.Cl. *C07C 67/31* (2006.01),
C07C 29/80 (2006.01), *C07C 67/02* (2006.01),
C07C 67/56 (2006.01), *C08G 18/36* (2006.01)

(71) Demandeurs/Applicants:
NARINE, SURESH, CA;
SPORNS, PETER, CA;
YUE, JIN, CA

(72) Inventeurs/Inventors:
NARINE, SURESH, CA;
SPORNS, PETER, CA;
YUE, JIN, CA

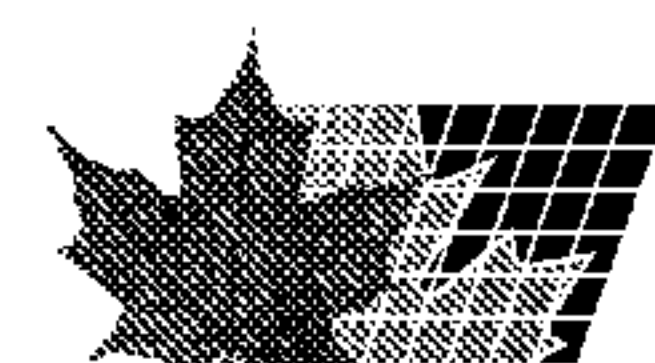
(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : BIOPLASTIQUES, LEURS MONOMERES, ET LEURS PROCEDES DE PREPARATION A PARTIR DE
SUBSTRATS AGRICOLES

(54) Title: BIOPLASTICS, MONOMERS THEREOF, AND PROCESSES FOR THE PREPARATION THEREOF FROM
AGRICULTURAL FEEDSTOCKS

(57) **Abrégé/Abstract:**

The present invention relates generally to polymers and monomers derived from agricultural feedstocks, and more particularly to methods for the production of monomers from renewable agricultural resources such as feedstocks, for example canola, flax and tallow, and polymers, in particular polyurethanes produced from such feedstocks. The present invention also relates to novel processes for the production of both monomers and polymers derived from such agricultural feedstocks.



Abstract of the Disclosure

The present invention relates generally to polymers and monomers derived from agricultural feedstocks, and more particularly to methods for the production of monomers from renewable agricultural resources such as feedstocks, for example canola, flax and tallow, and polymers, in particular polyurethanes produced from such feedstocks. The present invention also relates to novel processes for the production of both monomers and polymers derived from such agricultural feedstocks.

Bioplastics, Monomers Thereof, and Processes for the Preparation Thereof from Agricultural Feedstocks

Background of the Invention

1. Field of the Invention

[0001] The present invention relates generally to monomers and polymers derived from agricultural feedstocks, and more particularly to methods for the production of monomers from renewable agricultural resources such as feedstocks, for example canola, flax and tallow, and polymers, in particular polyurethanes, produced from such monomers.

2. Brief Description of the Related Art

[0002] With the realization that oil resources are becoming increasingly hard to find and expensive to produce, many industries that use oil as their source of raw material are looking to other sources, preferably renewable sources. At present, the production of plastics is still mainly based on the use of oil resources and a very large subgroup (about 10%) of the plastics industry includes the production of various polyurethanes (American Plastics Council (<http://www.americanplasticscouncil.org>). Accessed April 10, 2005).

[0003] The preparation of polymers from renewable sources is of significant economic and scientific importance. As an inexpensive, readily available renewable resource, attention has been paid to renewable resources such as vegetable oils which are abundant and varied as a source for polymeric materials. Since they are composed of triacylglycerols containing predominantly unsaturated fatty acids, native North American vegetable oils are chemically relatively unreactive. But other functional groups such as hydroxyl, epoxy, or carboxyl groups can be introduced at the positions of double bonds (Petrovic, Z.R., Guo, A.; Zhang, W., *J Polymer Sci A Polym. Chem* 38: 4602 (2000) to produce reactive raw materials, which have been utilized in producing valuable polymeric materials. Present methods of

using vegetable oils in polyurethane production require alcohol functionality to form what are widely referred to as polyols.

[0004] Vegetable oils are predominantly made up of triacylglycerol molecules and have complex structures (O'Brien, R. D., *Fats and Oils: Formulating and Processing for Applications*, CRC press, Boca Raton, Florida, pp 16-17, 2004). Triacylglycerol molecules are constituted by three fatty acids (varying from 14 to 22 carbons each in length for North American seed oils) and connected to a glycerol backbone through ester linkages. The fatty acids constituting most common North American seed oils have 0 to 3 double bonds which provide the sites of reactivity to convert the triacylglycerol structure of the vegetable oil into a triacylglycerol polyol, the raw material suitable for polymer production. Some triacylglycerol oils such as castor and vernonia oils develop specialized functional hydroxyl or epoxy groups and the others (such as canola, flax or linseed oils) have a double-bond functionality which provides reaction sites which enables them to be processed into high-value biochemicals for various industries (Pryde, E.H., L. H. Privcen, and K. D. Mukherjee (Eds.), *New Sources of Fats and Oils*, American Oil Chemists Society, Champaign, IL, 1981).

[0005] In polymer applications, certain grades of vegetable oils and their derivatives, such as polyol products, have been industrially explored as an alternative feedstock to produce additives or components for composites or polymers with definite advantages when compared with fossil and mineral raw materials (Pryde, E.H., L. H. Privcen, and K. D. Mukherjee (Eds.), *New Sources of Fats and Oils*, American Oil Chemists Society, Champaign, IL, 1981).

[0006] In the polymer field (which includes materials such as poly vinyl chloride (PVC) and polyurethane, and the like), plant oils based materials with varying physical, mechanical and thermal properties have been produced (Salunkhe, D. K., J. K. Chavan, R. N. Adsule, S. S. Kadam, in *World Oilseeds: Chemistry, Technology, and Utilization*; Van Nostrand Reinhold, New York, pp 87-89, 1992; John, J., M. Bhattacharya and R. B. Turner, Characterization of polyurethane foams from soybean oil, *J. Appl. Polym. Sci.* 86, 3097-3107 (2002); Khot, S. N., J. J. Lascalea, E. Can, S. S. Morye, G. I. Williams, G. R. Palmese, S. H. kusefoglu and R. P. Wool, Development and application of triglyceride-based

polymers and composites, *ibid.* 82: 703-723 (2001)), but much more needs to be done to widen the pool of biochemical feedstock, enhance the yields, optimize the processes, and broaden the products.

[0007] Polyurethanes which have a wide range of applications (elastomers, rigid set resins, flexible slab, and foams) are traditionally industrially produced by reacting petroleum based polyols with isocyanates (Szycher, M., *Szycher's Handbook of polyurethanes*, CRC Press, Boca Raton, FL., 1999). In recent years, naturally functionalized triacylglycerol oils (Barrett, L.W., L.H. Sperling, C.J. Murphy, Naturally functionalised triglyceride oils in interpenetrating polymer networks. *J. Am. Oil Chem. Soc.* 70: 523– 534 (1993); Carlson K.D. and S.P. Chang, Chemical epoxidation of a natural unsaturated epoxy seed oil from *Vernonia galamensis* and a look at epoxy oil markets., *ibid.* 62: 934–939. (1985)) as well as vegetable oil polyols have attracted attention for making a multitude of plastic products including various polyurethanes (PUs) (Khoe, T. H., F.H. Otey, and E.N. Frankel, Rigid urethane foams from hydroxymethylated linseed oil and polyol esters, *ibid.* 49: 615-618 (1972); Lyon, C.K., V. H. Garret and E. N. Frankel, Rigid urethane foams from hydroxymethylated castor oil, safflower oil, oleic safflower oil, and polyol esters of castor acids., *ibid.* 51: 331-334 (1974); Guo, A., Y. Cho and Z. S. Petrovic, Structure and properties of halogenated and nonhalogenated soy-based polyols., *J. Polym. Sci: Part A: Polym. Chem.* 38: 3900-3910 (2000); Guo, A., D. Demydov, W. Zhang and Z.S. Petrovic, Polyols and polyurethanes from hydroformylation of soybean oil., *J. Polym. & Environ.* 10: 49-52 (2002); Hu, Y.H., Y. Gao, D. N. Wang, C. P. Hu, S. Zu. L. Vanoverloop and D. Randall, Rigid polyurethane foam prepared from a rape seed oil based polyol., *J. Appl. Poly. Sci.*, 84: 591-597 (2002); Dwan'Isa, J.-P. Latere, A.K. Mohanty, M. Misra, L.T. Drzal and M. Kazemizadeh, Novel Biobased Polyurethanes Synthesized from Soybean Phosphate Ester Polyols: Thermomechanical Properties Evaluations., *J. Polym. & Environ.* 11: 161-168 (2003)).

[0008] The alcohol functionality also can already be found in some natural oils such as castor oil (Saxena, P.K., S.R. Srinivasan, J. Hrouz, and M. Ilavsky, The Effect of Castor Oil on the Structure and Properties of Polyurethane Elastomers, *J. Appl. Polym. Sci.* 44: 1343-1347 (1992)).

[0009] Alternately research groups have sought to introduce alcohol functionality utilizing the reactivity of double bonds to hydroformylate (Lyon, C.K., V.H. Garret, and E.N. Fankel, Rigid Urethane Foams from Hydroxymethylated Castor-oil, Safflower Oil, Oleic Safflower Oil and Polyol Esters of Castor Acids, *J. Am. Oil Chem. Soc.* 51(8): 331-334 (1974)) or introduce epoxides that can later be opened in various ways (Hu, Y.H., Y. Gao, D.N. Wang, C.P. Hu, S. Zu, L. Vanoverloop, and D. Randall, Rigid Polyurethane Foam Prepared from a Rape Seed Oil Based Polyol, *J. Appl. Polym. Sci.* 84: 591-597 (2002)).

[0010] For example, Frankel and group (Khoe, T. H., F. H. Otey, and E. N. Frankel, Rigid urethane foams from hydroxymethylated linseed oil and polyol esters, *J. Am. Oil. Chem. Soc.* 49: 615-618 (1972); Lyon, C. K., V. H. Garret and E. N. Frankel, Rigid urethane foams from hydroxymethylated castor oil, safflower oil, oleic safflower oil and polyol esters of castor acids, *Ibid.* 51: 331-334 (1974)) have produced derivatives of castor, safflower, and flax oils with enhanced hydroxyl groups, and Petrovic and group (Guo, A., D. Demydov, W. Zhang, and Z. S. Petrovic, Polyols and polyurethanes from hydroformylation of soybean oil, *J. Polym. & Environ.* 10- 49-52 (2002)) have produced soybean oil based polyols.

[0011] The second method involves epoxidation of unsaturated fatty acids followed by alcoholysis reactions to introduce hydroxyl functionality. Petrovic and his group have successfully used it to produce polyols from soybean oil (Guo, A., Y. Cho, and Z. S. Petrovic, Structure and properties of halogenated and nonhalogenated soy-based polyols, *J. Polym. Sci: Part A: Polym. Chem.* 38: 3900-3910 (2000)). Hu and coworkers (Hu, Y. H., Y. Gao, D. N. Wang, C. P. Hu, S. Zu, L. Vanoverloop and D. Randall, Rigid polyurethane foam prepared from a rape seed oil based polyol, *J. Appl. Polym. Sci.* 84: 591-597 (2002)) have used this reaction to produce polyols from canola oil. The above technologies yielded heterogeneous triacylglycerol polyols with hydroxyl functionality situated in the middle of the fatty acid chains, causing significant steric hindrance during crosslinking reactions in the production of polymers.

[0012] However, the polyols produced so far by the reported technologies have their hydroxyl groups located in the middle of the triacylglycerol fatty acid chains leaving pendant chains of the triacylglycerol (also known as dangling chains) unsupported, which significantly limits the rigidity of the resulting polyurethanes. Significant steric hindrance

to crosslinking (especially by bulky aromatic diisocyanates) are introduced by the –OH groups being located in the middle of the fatty-acid moieties, leading to less than optimized cross-linking density. Moreover, these dangling chains which are imperfections in the final polymer network, do not support stress if the network is under load and act as plasticizers which reduce the polymer rigidity and increase its flexibility.

[0013] Ozonolysis was used to obtain polyols with terminal primary hydroxyl groups and different functionalities from trilinolein, low-saturation canola oil, and soybean oil (Petrovic, Z. S., W. Zhang, and I. Javni, Structure and properties of polyurethanes prepared from triacylglycerol polyols by ozonolysis, *Biomacromolecules*, 6: 713-719 (2005)).

[0014] It has been shown that polyurethanes produced using vegetable oils present some excellent properties such as enhanced hydrolytic and thermal stability, as shown with soybean oil based PUs (Zlatanic, A., A. S. Petrovic and K. Dusek, Structure and Properties of Triolein-Based Polyurethane Networks., *Biomacromolecules*, 3: 1048-1056 (2002)).

[0015] In terms of other useful materials derived from feedstocks, estolides are dimers formed by a normal fatty acid esterifying a hydroxy fatty acid. Estolides synthesized from vegetal oils (Cermak S.C., Isbell T.A., Synthesis of estolides from oleic and saturated fatty acids *J. Am. Oil Chem. Soc.* 78 (6): 557-565 (2001)) are new functional fluids and have a rapidly growing importance in cosmetics, coatings, and biodegradable lubricants.

[0016] In view of the above, there remains a need for novel methods for the production of monomers and polymers having terminal hydroxyl functional groups from renewable resources, such as feedstocks. In particular, the use of renewable feedstocks, such as vegetable oils including canola and flax, to produce monomers capable of producing high-quality polymers, such as polyurethane foams and elastomers, utilizing reactions which are easily and inexpensively performed at an industrial scale would be highly desirable. The development of novel methods of producing estolides is also highly desirable.

Summary of the Invention

[0017] Included in the scope of the invention is a method of introducing terminal hydroxyl functionality by way of ozonolysis of double bonds found in renewable feedstocks, followed by reduction to afford hydroxyl containing monomers, useful in the production of polymers, in particular, polyurethanes, and the like.

[0018] Therefore, included within the scope of the invention is a method for the production of a polyol from a renewable feedstock comprising one or more unsaturated fatty acid triacylglycerols, wherein the method comprises the steps of:

- (a) ozonolysis of two or more double bonds in the unsaturated fatty acids found in the triacylglycerols of the feedstock under conditions effective to afford two or more corresponding ozonides; and
- (b) reductive hydrogenation under conditions effective to afford hydrogenation of the products of step (a) to afford one or more corresponding polyols,

wherein the one or more polyols comprise a triacylglycerol containing at least two primary hydroxyl groups.

[0019] In yet another aspect of the present invention the method for the production of a polyol from a renewable feedstock further comprises the step of separating the one or more polyols from the reaction mixture of step (b) under conditions suitable to separate the polyols.

[0020] In yet another aspect of the present invention there is provided a method for producing a polyurethane polymer which comprises reacting a polyol prepared by the methods of the present invention with a suitable isocyanate to afford the polyurethane polymer.

[0021] In yet another aspect of the present invention is a polyurethane polymer prepared from a polyol prepared by the process of the present invention and an isocyanate.

[0022] In yet another aspect of the present invention is provided a method for the production of nonanol, hexanol, propanol, and 1,3-propanediol from a renewable feedstock comprising a fatty acid triacylglycerol having at least one unsaturated fatty acid chain, the method comprising the steps of:

- (a) ozonolysis of the double bonds in the fatty acid chain of the triacylglycerol of the feedstock;
- (b) reductive hydrogenation of the ozonide product formed in step (a) to produce nonanol, hexanol, propanol, and 1,3-propanediol.

[0023] In yet another aspect of the present invention is provided a method for the production of an estolide from a renewable feedstock comprising one or more unsaturated fatty acid triacylglycerols, wherein the method comprises the steps of:

- (a) ozonolysis of the double bonds in the unsaturated fatty acids found in the triacylglycerols of the feedstock;
- (b) reductive hydrogenation of the products of step (a) to produce the corresponding polyol in the presence of a short chain alcohol;

wherein the polyol comprises a triacylglycerol containing at least one terminal hydroxyl group, and wherein the reaction conditions are sufficient to afford transesterification between the polyol and the short chain alcohol, thereby affording said estolide.

[0024] In yet another aspect of the present invention there is provided an improved apparatus for carrying out ozonolysis reactions, the improvement comprising:

a longitudinally disposed agitator operatively connected to a motor, the longitudinally disposed agitator comprising a plurality of pitched blades,

wherein the longitudinally disposed agitator extends downwardly into a reaction vessel having an upper and a lower end,

the reaction vessel comprising an ozone inlet channel disposed at the lower end and extending across the diameter of the reaction vessel,

the ozone inlet channel having two apertures for ozone input at opposing ends thereof and a plurality of pores for release of ozone into the reaction vessel.

[0025] In still another aspect of the present invention, the method for the production of a polyol from a renewable feedstock further comprises the selection of ozonolysis conditions in order to produce polyols for forming polyurethane products having harder or softer properties. In another aspect of the present invention, the ozonolysis conditions comprise at least one of ozonolysis time, ozone flow rate, and concentration of the renewable feedstock.

[0026] Numerous advantages are afforded by this route of modifying renewable feedstocks such as vegetable oils via ozonolysis of double bonds found in renewable feedstocks, followed by reduction to produce polyols. Methods of the present invention based on ozonolysis and hydrogenation for the production of polyols from unsaturated triacylglycerols afford polyol products and can introduce terminal multiple alcohol functional groups into the triacylglycerol that can then be used as a starting material for the production of polyurethane products. The polyols so produced locates the hydroxyl functionality at the terminal end of the fatty acid chain, greatly enhancing reactivity and reducing steric hindrances to crosslinking molecules.

[0027] These and other aspects will become apparent upon reading the following detailed description of the invention and by reference to the following figures.

Brief Descriptions of the Drawings

[0028] **Figure 1** is a schematic representation of the production of polyols and subsequent interesterification reactions as described in Example 1;

[0029] **Figure 2** depicts the processes of the present invention with triolein found in Canola oil as a starting material to illustrate the production of polyols;

[0030] **Figure 3** is an HPLC of Reaction Mixture (upper trace) and Fraction 76 (lower trace) after Hydrogenation;

[0031] **Figure 4** is an NMR Comparison of Fraction 76 and Tristearin;

[0032] **Figure 5** shows the electrospray Ionization Mass Spectrometry of Fraction 76;

[0033] **Figure 6** shows a Thin Layer Chromatography plate of products after ozonolysis as described in Example 2;

[0034] **Figure 7** is a gas chromatogram of first and second hydrogenation products of Example 2; (A) is a chromatogram of the product after the first hydrogenation step; (B) is a chromatogram of the product after the second hydrogenation step;

[0035] **Figure 8** illustrates various side products obtained in the reaction described in Example 2;

[0036] **Figure 9** shows GC chromatographs recorded before and after distillation step of Example 2;

[0037] **Figure 10** shows an HPLC chromatogram of the polyol product of Example 2;

[0038] **Figure 11** shows HPLC chromatograms of samples of product of Example 2;

[0039] **Figure 12** shows FTIR spectra of samples of product of Example 2;

[0040] **Figure 13** shows the NMR spectra of samples of product of Example 2;

[0041] **Figure 14** shows mass spectra of samples of product of Example 2;

[0042] **Figure 15** shows possible products of transesterification reactions including the production of estolides of Example 6;

[0043] **Figure 16** shows the mass spectra of products of the transesterification reactions of Figure 15;

[0044] **Figure 17** is a GC graph of Canola based reaction products, ozonized at 0°C with air as a supply gas for 8h. (a) before distillation. (b) after distillation;

[0045] **Figure 18** is an FTIR spectra of: (a) Canola oil (b) Flax oil (c) Canola-air polyol (d) Flax-air polyol (e) Canola-oxygen polyol; **Figure 18a** is an FTIR spectra in the range 400-4000 cm^{-1} ; **Figure 18b** is an enlargement of the FTIR band at 1650 cm^{-1} characteristic of C=C double bond; **Figure 18c** is an enlargement of the FTIR band at 3006 cm^{-1} characteristic of unsaturated C-H stretches;

[0046] **Figure 19** is an HPLC chromatography of Canola-air polyol, ozonized for 8h at 0°C;

[0047] **Figure 20** represents DSC curves of: (a) Canola oil (b) Flax oil (c) Canola-air polyol (d) Flax-air polyol (e) Canola-oxygen polyol and (f) Hydrogenated Canola oil; **Figure 20a** shows crystallization curves; **Figure 20b** shows melting curves;

[0048] **Figure 21** illustrates the viscosity of: (a) Flax oil (b) Canola oil, (c) Canola-air polyol, (d) Flax-air polyol, (e) Canola-oxygen polyol; **Figure 21a**) illustrates viscosity as a function of time; **Figure 21b**) illustrates viscosity as a function of temperature;

[0049] **Figure 22** is an FTIR spectra of an elastomer with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU);

[0050] **Figure 23** shows reversing heat flow vs. temperature of elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU);

[0051] **Figure 24** illustrates thermomechanical analysis curves of an elastomer with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU);

[0052] **Figure 25** illustrates the Storage moduli of elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU);

[0053] **Figure 26a** shows the TGA of an elastomer with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c)

soybean oil based polyurethane (SOBPU); **Figure 26b** shows Derivative TGA curves of an elastomer with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU);

[0054] **Figure 27** graphically illustrates the nominal stress-strain of elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU), (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU)

[0055] **Figure 28** is an FTIR spectra of polyurethane foams (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (— — —) Castor oil based polyurethane (Castor-PU);

[0056] **Figure 29a** illustrates the Storage moduli of polyurethane foams. Insert: first derivatives relative to temperature of storage moduli; **Figure 29b** illustrates the Loss moduli; **Figure 29c** illustrates the $\tan \delta$; of (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (— — —) Castor oil based polyurethane (Castor-PU);

[0057] **Figure 30a** is TGA curves of polyurethane foams in nitrogen ; **Figure 30b** represents derivative TGA curves of canola and soybean oil based polyurethane foams; (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (— — —) Castor oil based polyurethane (Castor-PU);

[0058] **Figure 31** shows the compressive strength vs. strain of polyurethane foams (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (— — —) Castor oil based polyurethane (Castor-PU);

[0059] **Figure 32a** is a scanning electron micrograph of the Canola oil based polyurethane (Canola-PU); **Figure 32b** is a scanning electron micrograph of the Soybean oil based polyurethane (Soybean-PU); **Figure 32c** is a scanning electron micrograph of the Castor oil based polyurethane (Castor-PU);

[0060] **Figure 33** is a HPLC of polyols produced with Pd-C , Raney Ni System;

[0061] **Figure 34** is a HPLC of polyols produced with Zinc, Raney Nickel System;

[0062] **Figure 35** is a HPLC of polyols produced with Recycled Ethyl Acetate

[0063] **Figure 36(a)** represents the Viscosity as a function of time of: (a) Ethyl Acetate Canola Oil Based Polyols, (b) Recycled Ethyl Acetate Canola Oil Based Polyols. **Figure 36(b)** represent the Viscosity as a function of temperature of: (a) Ethyl Acetate Canola Oil Based Polyols, (b) Recycled Ethyl Acetate Canola Oil Based Polyols;

[0064] **Figure 37(a)** represents the Storage moduli of polyurethane foams. **Figure 37(b)** represents the Loss moduli. **Figure 37(c)** represents the Tan δ of polyurethane foams. (a) Ethyl Acetate Canola Oil Based PU (EACOBPU) and (b) Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU);

[0065] **Figure 38** represent the Compressive strength vs. strain of polyurethane foams. (a) Ethyl Acetate Canola Oil Based PU (EACOBPU) and (b) Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU)

[0066] **Figure 39** shows a schematic of one embodiment of a reactor for use with the ozonolysis processes of the present invention.

[0067] **Figures 40(a)** and **40(b)** illustrate the agitator blades of the ozonolysis reactor and their angle of attachment to the agitator rod in accordance with one embodiment of the present invention.

[0068] **Figure 41** illustrates a prior art ozonolysis reactor.

Detailed Description of Embodiments

[0069] The present invention provides novel, versatile and efficient processes and conditions for the preparation of monomers and polymers useful in the preparation of plastics and the like.

[0070] The present invention also provides a method of introducing hydroxyl functionality by way of ozonolysis of double bonds found in renewable feedstocks, followed by reduction

to afford hydroxyl containing monomers, useful in the production of polymers, in particular, polyurethanes.

[0071] The present invention also provides a method for the production of a polyol from a renewable feedstock comprising one or more unsaturated fatty acid triacylglycerols, wherein the method comprises the steps of:

- (a) ozonolysis of two or more double bonds in the unsaturated fatty acids found in the triacylglycerols of the feedstock under conditions effective to afford two or more corresponding ozonides; and
- (b) reductive hydrogenation under conditions effective to afford hydrogenation of the products of step (a) to afford one or more corresponding polyols,

[0072] wherein the one or more polyols comprise a triacylglycerol containing at least two primary hydroxyl group.

[0073] The present invention also provides a method for the production of a polyol from a renewable feedstock further comprising the step of separating the one or more polyols from the reaction mixture of step (b) under conditions suitable to separate the polyols.

[0074] In one embodiment, the one or more polyols produced are isolated in greater than 90% purity relative to non-polyol components contained in or produced during the production of the one or more polyols. In another embodiment, the one or more polyols produced are isolated in greater than 95% purity relative to non-polyol components contained in or produced during the production of the one or more polyols.

[0075] The present invention also provides a method for producing a polyurethane polymer which comprises reacting a polyol prepared by the methods of the present invention with a suitable isocyanate to afford the polyurethane polymer.

[0076] The present invention also provides a method for the production of nonanol, hexanol, propanol, and 1,3-propanediol from a renewable feedstock comprising a fatty acid triacylglycerol having at least one unsaturated fatty acid chain, the method comprising the steps of:

- (a) ozonolysis of the double bonds in the fatty acid chain of the triacylglycerol of the feedstock;
- (b) reductive hydrogenation of the ozonide product formed in step (a) to produce nonanol, hexanol, propanol, and 1,3-propanediol; and
- (c) separating nonanol, hexanol, propanol, and 1,3-propanediol from the hydrogenated product formed in step (b) by wiped-blade molecular distillation.

[0077] The present invention also provides a method for the production of an estolide from a renewable feedstock comprising one or more unsaturated fatty acid triacylglycerols, wherein the method comprises the steps of:

- (a) ozonolysis of the double bonds in the unsaturated fatty acids found in the triacylglycerols of the feedstock;
- (b) reductive hydrogenation of the products of step (a) to produce the corresponding polyol in the presence of a short chain alcohol;

wherein the polyol comprises a triacylglycerol containing at least one terminal hydroxyl group, and wherein the reaction conditions are sufficient to afford transesterification between the polyol and the short chain alcohol, thereby affording said estolide.

[0078] The present invention also provides novel polyurethane polymers prepared from a polyol prepared by the process of the present invention and an isocyanate.

[0079] The present invention also provides an improved apparatus for carrying out ozonolysis reactions, the improvement comprising:

a longitudinally disposed agitator operatively connected to a motor, the longitudinally disposed agitator comprising a plurality of pitched blades,

wherein the longitudinally disposed agitator extends downwardly into a reaction vessel having an upper and a lower end,

the reaction vessel comprising an ozone inlet channel disposed at the lower end and extending across the diameter of the reaction vessel,

the ozone inlet channel having two apertures for ozone input at opposing ends thereof and a plurality of pores for release of ozone into the reaction vessel.

[0080] In one embodiment, the method for the production of a polyol from a renewable feedstock further comprises the selection of ozonolysis conditions in order to produce polyols for forming polyurethane products having harder or softer properties. In another embodiment, the ozonolysis conditions comprise at least one of ozonolysis time, ozone flow rate, and concentration of the renewable feedstock.

[0081] Therefore, in one embodiment of the present invention is provided a method for the production of polyols from unsaturated fatty acid triacylglycerols (TAGs) such as those depicted in **Figure 1**. Such polyols can then be used as a starting material for the production of polyurethane products with appropriate isocyanate crosslinkers (M. Szycher, Isocyanate Chemistry, in *Szycher's Handbook of Polyurethanes*, CRC Press, New York, pp. 4-1 to 4-40, 1999).

[0082] In one embodiment, the method to produce the polyols includes ozonolysis of the double bonds in unsaturated fatty acids found in the triacylglycerols, followed by a reductive hydrogenation to produce the corresponding polyol. This sequence of reactions can afford several advantages over other approaches to produce alcohol functional groups in triacylglycerols. While highly unsaturated vegetable oils such as canola or flaxseed contains many different unsaturated fatty acids, the first double bond for all of these fatty acids is always found at carbon nine. In addition these vegetable oils contain a very small percentage of saturated fatty acids (D. Firestone, Physical and Chemical Characteristics of Oils, Fats, and Waxes. AOCS Press, 1999). Thus, the polyol formed, be it a monohydroxyl functionalized triacylglycerol (also referred to as a mono-ol), dihydroxyl functionalized triacylglycerol (also referred to as a diol), or trihydroxyl functionalised triacylglycerol (also referred to as a triol), from such highly unsaturated vegetable oils is more homogeneous than the starting triacylglycerols in the case where the triacylglycerol comprises different unsaturated fatty acids all resulting in the same primary alcohol upon ozonolysis and subsequent reductive hydrogenation. In addition the primary alcohols formed at the C9

group of the fatty acid triacylglycerol chains are reactive primary alcohols, with the chance of forming a single alcohol group on a triacylglycerol (chain terminators) very low.

[0083] As used in the context of the present invention, the various chemical terms are to be given their ordinary meaning as would be understood by persons skilled in the art, unless provided otherwise.

[0084] The term “polyol” as used in the context of the present invention is meant to include triglycerides having a hydroxyl functionality in at least two of the three chains within the triacylglycerol. Accordingly, “diol”, and “triol” as used herein are meant to refer to those triacylglycerols having two and three hydroxyl functionalities present in the triacylglycerol, respectively, and are meant to be included in the term “polyol”.

[0085] To demonstrate this method, ozonolysis and hydrogenation of triolein was undertaken to produce a triol product with primary alcohol functional groups at position nine of each fatty acid ester in the original triacylglycerol. Further details regarding methods for carrying out the procedure are set out in **Example 1** below and as described below.

[0086] To prevent any potential complications, reaction conditions are chosen to avoid increasing the molecular complexity of the products formed. For example, in one embodiment the ozonolysis is alternated with nitrogen flushing so that the production of acid groups is minimized. Acid groups are detrimental to the polyurethane forming process (M. Szycher, Isocyanate Chemistry, in *Szycher's Handbook of Polyurethanes*, CRC Press, New York, pp. 4-1 to 4-40, 1999). Also as described in **Example 1** below, in one embodiment the hydrogenation step is carried out twice to insure that no unreacted double bonds would remain in the final product.

[0087] Additional products are afforded by the present methods for the preparation of polyols. For example, **Figure 2** further illustrates various potential products that may be formed when triolein is used as a starting material for methods of the present invention.

[0088] Thus, the present invention further includes methods for the preparation of polyols that include the separation of the polyol products formed after these reactions. The methods for separation which can be used can be any method which allows for the separation of the

polyol products. In one embodiment, methods to separate the polyol products on the basis of the number of alcohol functional groups may be used such as with the use of diol derivatized silica gel. Other separation methods known to those skilled in the art, such as flash chromatography or gel permeation chromatography, for example, may also be used.

[0089] In one embodiment, the method of Elfman-Borjesson and Harrod (Elfman-Borjesson, I. and M. Harrod, Analysis of Non-Polar Lipids by HPLC on a Diol Column. *J. High Resol. Chromatogr.* 20: 516-518 (1997)) is modified to give the required chromatography. The use of the diol column [Betasil Diol-100 (5 μ m particle size) 250 $\times$ 4 mm] provides that lipid materials are separated on the basis of the number of alcohol functional groups present in the triacylglycerol. Using the diol column, unreacted triacylglycerol was observed to have the shortest retention time; followed by triacylglycerols with a single alcohol group; then two alcohol groups and finally the longest retained material on the column was that that contained three alcohol groups. As can be seen in **Figure 3**, the major product of the reactions (peak at 14.2 minute retention time) appeared in the region (longest retention time) where a triacylglycerol containing three alcohol groups would appear. When the peaks were integrated, the peak at 14.2 retention time made up about one third (33.9%) of the total material.

[0090] To further confirm the reaction products, a larger amount of product material for spectral analysis was isolated using silica gel derivatized with diol groups. Column chromatography using a larger mesh material was carried out. The fractions isolated were analyzed using thin layer chromatography and those containing larger amounts of material were subjected to our HPLC analysis. One of the purer fractions (fraction 76, see **Figure 3**) was evaporated and analyzed extensively using NMR (**Figure 4**) and mass spectrometry (**Figure 5**). This purified material corresponded to the major product that was noted in the final reaction mixture.

[0091] The proton NMR of this purified fraction (**Figure 4**) was observed to be very close to the anticipated "triol" compound of **Figure 1**. but there seemed to be an excess of protons for the fatty alcohol ester groups and there was an NMR unexplained triplet at 4.05 ppm. However on the positive side a comparison with the proton NMR of tristearin indicated many of the expected proton shifts. The methyl protons of tristearin (0.95 ppm) were not

present in the fraction 76 NMR. Moreover there was a new triplet at 3.65 ppm that was in the region expected for protons on methylene alcohol groups. Also the pattern of the glycerol proton peaks at 5.27, 4.30 and 4.16 ppm were virtually identical to the coupling pattern seen in tristearin. The presence of the triol in the purified fraction 76 was confirmed by accurate mass spectroscopy.

[0092] While not wishing to be bound by any particular theory, experimenting with structural variations using estimates found in ChemDraw (ChemDraw Ultra, Version 8, CambridgeSoft Corporation, MA, USA) gave a likely explanation for the impurity observed in both the NMR and seen in the HPLC. The unexplained triplet at 4.05 ppm could be explained by compound A (**Figure 1**) produced as a result of interestification. This would also explain the excess fatty alcohol ester protons. The conditions for interesterification in the reaction conditions of Example 1 were ideal with some acid formed as a result of the ozonolysis and the final reaction products containing numerous reactive primary alcohols. Moreover, it is preferable that alcohols such as methanol and ethanol are to be avoided as solvents of the reactions of the present invention as significant transesterification to the methyl and ethyl esters could be effected. To further confirm the interesterification reaction, electrospray mass spectroscopy (**Figure 5**) indicated the expected mass peaks for the triol (protonated form at 561.4, sodium form at 583.4), but also higher mass peaks at 717.6 and 739.6 which corresponded to the protonated and sodium form of compound A of **Figure 1**. In addition there was also a small peak at 427.3 that was likely indicative of the sodium form of compound B (**Figure 1**). It could also not be ruled out that the interesterification reaction occurred to some extent during sample preparation for spectral analysis.

[0093] As such, another important aspect of the present invention is that even when interesterification is observed under certain reaction conditions, one of the products of interesterification also contains hydroxyl terminal functionalities that are available for crosslinking with isocyanate groups. The introduction of multiple alcohol functional groups into the triacylglycerol is important so that chain-terminating triacylglycerols with only a single alcohol are not present to a significant extent.

[0094] In the present invention, the renewable feedstock that may be used for the production of polyols is any which contains unsaturated fatty acid triacylglycerols which allow for the formation of the polyol products using the methods of the present invention. In one embodiment, polyols may be prepared from feedstocks such as unsaturated seed oils, for example canola, which in turn may be used, inter alia, in the production of polyurethane products. Canola vegetable oil contains more than 90% of unsaturated fatty acids, including oleic acid, linoleic acid and linolenic acid (D. Firestone, Physical and Chemical Characteristics of Oils, Fats, and Waxes. AOCS Press, 1999), which all have a double bond at carbon nine. Other feedstocks which contain some degree of unsaturated fatty acids and therefore may be used for the production of polyols include linseed, sunflower, tung, lesquerella, flaxseed, Jatupha, camelina sativa, hump, peanut, palm, soy, cottonseed, corn, cashew nuts, calendula, mustard, sesame, safflower, sunflower, rapeseed, olive, castor, jojoba, brazil nuts, avocado, and kenaf oils.

[0095] Methods of the present invention also afford a variety of products besides the polyols of the present invention. Such additional products depend in part upon the starting renewable feedstock. In particular, depending on the feedstock, a number of short straight chain alcohols may also be produced by the methods of the present invention. Short chain alcohols are potential chain-terminators in reactions using isocyanates to crosslink the polyol compounds, and may serve to promote interesterification of the polyols, which can result in increasing heterogeneity of the polyol feedstock, or in the formation of chain-terminating compounds.

[0096] Accordingly, in one embodiment, such short chain alcohols are removed from the polyols. In one embodiment, the short chain alcohols are removed using wiped-blade molecular distillation.

[0097] GC may be used to identify and quantify the short-chain alcohols. Column chromatography may be used to separate pure mono-ol, diol and triol, and then ^1H and ^{13}C NMR as well as mass spectrometry may be used to uniquely identify these products once the short chain alcohols are removed from the reaction mixtures. Such an identification procedure facilitates the use of a simple HPLC method to determine the composition of

mixtures of polyol product, for use as a quality-control mechanism in designing novel polyol feedstock.

[0098] Solvents for use in the present ozonolysis and hydrogenation reactions are those that afford production of the polyol products. In one embodiment, the solvents for hydrogenation comprise ethyl acetate. Ethyl acetate is a comparatively benign solvent for use in an industrial setting.

[0099] To further illustrate the flexibility of the present methods with different renewable feedstocks as starting materials, details surrounding a preferred embodiment for this process using canola oil as a starting material follow, additional details of which are set out in **Example 2** below.

[00100] Different analysis methods may be used to determine the products formed after each step of the reactions. In one embodiment, after ozonolysis was complete, TLC plates are run on the organic layer, the aqueous layer, as well as the starting material, with the developing solvent being 10% of ethyl acetate in hexane (**Figure 6**). As can be seen from **Figure 6**, for the same retention factor (R_f) value of 0.6, the spot for the organic fraction became much smaller than that of the glycerides in the canola oil and another spot showed up on the base line. It demonstrated that most of the triacylglycerols in the canola oil reacted with ozone to produce ozonide, which was much more polar than the TAGs.

[00101] In the present embodiment using canola oil as the starting material, nonanol is produced as a side product only when the double bonds between carbon 9 and carbon 10 were broken and the ozonide of the short nine carbon chain cleaved from the TAG was completely reduced by hydrogen. Otherwise, some nonanal would still remain in the hydrogenation product.

[00102] Based on this, the presence of nonanal, easily tested by GC, may be used as an indicator of the completion of hydrogenation. The second hydrogenation step was performed because a significant amount of nonanal was detected after the first hydrogenation (**Figure 7**, curve A). This ensured that the ozonide and the double bonds were almost completely reduced as evidenced by the nonanal peak which almost disappeared after the second hydrogenation as shown in **Figure 7**, curve B. Therefore, the

reaction conditions for the hydrogenation reaction of the present invention can be any operable conditions which yield the desired polyol product and, if desired, the maximum quantity of nonanol bi-product. A preferred temperature range for the hydrogenation processes is from about 120°C to about 140°C, although this temperature can be higher or lower depending upon the reagents, reaction conditions and the solvent used. Typical reaction times for the ozonolysis and hydrogenation reactions are between 2 and 3 hours, although longer or shorter times may be used if necessary.

[00103] In addition to nonanol, other short chain side products were produced and purified by the methods of the present invention, such as the small chain mono alcohols, propanol and hexanol, as illustrated in **Figure 8**. Such separation procedure is desired because, on one hand, all these small side products are potential chain terminators to the cross-linking reactions in the production of polyurethanes and on the other hand, they are very valuable materials in the chemical industry. As such, another aspect of the present invention is a method for the production and purification of by-products from the present processes. In one embodiment, wiped blade molecular distillation may be utilized to separate the short chain molecules from the triacylglycerol polyols as described herein. Further separation of the short chain by-products by conventional techniques such as distillation and crystallization may be carried out. GC chromatographs recorded before and after distillation demonstrated that the end-product polyols were substantially free of short-chain by products except of a small amount of nonanol, i.e. <1% as shown in **Figure 9**.

[00104] After the short chain by-products were removed from the polyols by wiped blade molecular distillation, in one embodiment, an HPLC analysis method modified from Elfman-Borjesson and Harrod (Elfman-Borjesson, I. and M. Harrod, Analysis of Non-Polar Lipids by HPLC on a Diol Column. *J. High Resol. Chromatogr.* 20: 516-518 (1997)) was developed to separately identify the different polyols. A special diol column [Betasil Diol-100 (5 µm particle size) 250×4 mm] was used to separate the polyols on the basis of the number of hydroxide groups present on the end of triacylglycerol chains, **Figure 10**. As four main peaks were separated, it was logical to assign them according to their position. Starting from the first with the shortest retention time, the peaks were assigned to the unreacted TAGs, followed by TAGs with a single alcohol group (mono-ol); then TAGs with two alcohol groups (diol) and finally TAGs with three alcohol groups (triol) the most

retained material, respectively. To further confirm the expected reaction products, flash chromatography was performed to separate the different polyols and TLC run on each fraction. Finally, fractions 28–50, 131–143, 264–289, 366–378 were respectively combined and named as samples A, B, C and D, and analyzed by HPLC, NMR, IR and Mass spectrometry.

[00105] As can be seen in **Figure 11**, each sample HPLC demonstrated a single peak with a retention time matching that of one of the four peaks shown in **Figure 10**, i.e. 4.04, 5.86, 15.94, and 30.92 min for samples A, B, C and D respectively.

[00106] The FTIR spectra of the four samples are shown in **Figure 12**. The 1650cm^{-1} characteristic C=C double bond stretch is reduced to very small bumps in all the spectra, confirming that almost all the double bonds in the canola oil have been reduced. The absorption band centered at 3300 cm^{-1} characteristic of hydroxyl group, is missing in the sample A, but appears in the samples B, C and D with a tendency to grow bigger and broader from B to D. This pattern qualitatively corroborate the peak assignments of **Figure 10** to the four main fractions i.e. TAG, mono-ol, diol, and triol.

[00107] The FTIR indications were quantitatively verified by ^1H -NMR. Two peaks in the ^1H -NMR of the samples (**Figure 13**), the triplet at 0.88 ppm representing the terminal methyl groups of the fatty acids, and the triplet at 3.60 ppm representing the methylene protons adjacent to hydroxyl group are very important and warrant careful attention. From sample A to D, there is a tendency for the methyl peaks to decrease and the methylene peaks to increase. For sample D, the peak representing the methyl protons has completely disappeared, and in Sample A, no peaks representing the methylene protons are present. This proves that sample A is the unreacted TAG with terminal methyl groups on the end of all three fatty acid chains. Similarly, D is proven to be the triol product with three hydroxyl groups present on the end of the chains (instead of the methyl groups) and according to the integrations of the methyl and methylene groups, sample B and C are mono-ol and diol products.

[00108] Mass spectroscopy provided additional strong evidence to further confirm the identity of the products. **Figure 14** shows that samples B, C and D have mass peaks at

803.7, 693.6, 583.4 respectively, which correspond to the protonated and sodium adducts of saturated mono-ol, diol and triol.

[00109] The short chain alcohols which were produced and separated in one embodiment as side products may be used as a solvent for hydrogenation, as set out in **Example 6** below. The resulting products were separated by wiped blade molecular distillation and flash chromatography then identified by MS and NMR. It was found that the polyol products were transesterified in the presence of nonanol and other short chain alcohols. The transesterification reaction involved here is shown in **Figure 15**. **Figure 16(a)** shows a mass peak at 427.3 corresponding to the protonated and sodium adduct of transesterified product I. **Figure 16(b)** shows a mass peak at 323.3 corresponding to the protonated and sodium adducts of the transesterified product II.

[00110] Importantly, the formed transesterification product II of **Figure 15** is an estolide, a member of a very important class of compounds used in lubricant, coatings, cosmetic, and hydraulic fluid applications. In its own right, the production of estolides such as those produced here, are of notable commercial importance, and it is of great significance to realize the potential of this reaction process to be tailored for the production of estolides. A generalized procedure for preparing estolides is set out in **Example 6** below.

[00111] For the purpose of polyurethane formation, however, it is of paramount importance to remove the short chain alcohol products, because not only they act as chain terminators, but also cause deterioration of the polyol product by transesterification. Clearly, the use of the recycled short chain alcohols as solvents is to be avoided in the production of polyols, as the transesterification degrades and makes more complex the glyceride polyol fraction after distillation. As such, an important aspect of the present invention is a method for the production of estolides. In another aspect of the present invention, the process may be tailored to produce an excess of estolides.

[00112] Another aspect of the present invention is the ability to readily optimize the processing conditions of the present invention to maximize triglyceride mono, diol and triol products by way of using different conditions. Furthermore, using novel processes of the present invention it is also possible to produce different “grades” of polyol products suitable for elastomers, rigid foams or flexible foams and the like with specific molecular profiles as

indicated by the unique mixture of triacylglycerol, mono-ol, diol and triol products by controlling the conditions of the claimed processes.

[00113] Therefore in another embodiment of the present invention, there is provided a method for the preparation of various grades of polyols from renewable resources, such as renewable feedstocks comprising oils such as canola and flax oils and the like, based on the ozonolysis and hydrogenation reactions of the present invention. Details of one embodiment of the present invention are further provided in **Example 3** below, and as follows. In particular, the dramatic effect of crystallization on polyol viscosities is evidenced by analyzing DSC measurements. This effect as expected diminished when the temperature increases. HPLC and GC measurements can be used to establish basic correlations between molecular diversity of the three types of polyols produced, and their physicochemical properties, such as hydroxyl number, acidity number, and viscosity.

[00114] In **Example 3** below, three grades of polyols were synthesized: (i) polyols from canola oil using oxygen gas supply to generate the ozone, and referred to as canola-oxygen; (ii) polyols from canola oil using air supply to generate the ozone, and referred to as canola-air; and (iii) polyols from flax oil using air supply to generate the ozone, and referred to as flax-air.

[00115] GC chromatographs recorded before and after distillation demonstrated that the end-product polyols were practically free of short-chain by-products apart from a small amount of nonanol (<1%) as illustrated in **Figure 17**, for a canola-air polyol sample. The GC chromatographs obtained for the other two grades of polyols also confirmed that the potential chain terminators of the cross-linking reactions which jeopardize the production of polyurethanes were removed effectively. High-value alcohols and acids such as nonanol and nonanoic acid were recovered with a relatively high yield in addition to hexanol and propanol. **Table 1** gives calculated and GC-determined experimental amounts of the 3-carbon derivatives (propanol and propionic acid), the 6-carbon derivatives (hexanol and hexanoic acid), and the 9-carbon derivatives (nonanol and nonanoic acid) of short chain by-product, in grams produced before distillation from 100g canola and flax oil. The calculations were based on the amount of TAGs (in 100g) compiled by Firestone (Firestone, D., Editor, In *Physical and Chemical Characteristics of Oils, Fats, and Waxes*, AOCS

press, Washington, D.C., 1999) for flax oil and by Neff et al. (Neff, W.E., T.L. Mounts, W.M. Rinsch, H. Konishi and M.A. El-Agaimi, Oxidative stability of purified canola oil triacylglycerols with altered fatty acid compositions as affected by triacylglycerol composition and structure, *J. Am. Oil Chem. Soc.* 71: 1101-1109 (1994)) for canola oil. The amount of the 9-carbon derivatives by-products was much higher than the others, implying that mostly it is the double bond functionality at carbon number nine which is cleaved.

Table 1: Calculated and experimental amounts in grams of short chain by-product from 100g canola and flax oil. (Errors are standard deviations, n = 3).

	Propanol equivalent	Hexanol equivalent	Nonanol equivalent	1,3 propanediol
Canola (theoretical)	1.70	7.46	28.60	10.00
Canola-air	0.44 ± 0.19	2.59 ± 0.29	11.85 ± 1.09	0.72 ± 0.21
Canola-oxygen	0.28 ± 0.06	4.09 ± 0.18	23.53 ± 0.32	0.59 ± 0.04
Flax (theoretical)	11.44	5.50	9.85	33.07
Flax-air polyol	0.49 ± 0.19	1.61 ± 0.54	5.92 ± 0.68	0

Propanol equivalent includes the 3-carbon derivatives (propanol and propionic acid); hexanol equivalent includes the 6-carbon derivatives (hexanol and hexanoic acid), and nonanol equivalent includes the 9-carbon derivatives (nonanol and nonanoic acid).

[00116] The production of separate primary alcohols demonstrates that the ozonolysis and hydrogenation reactions effectively cleave the double bonds and add hydroxyl functionality to both of the severed ends. Furthermore, depending on the processing conditions, more or less of the double bonds can be cleaved. This places significant power in the hands of the process engineer, as one can therefore tailor the process to prepare “designer” polyols which impart specific and desirable physical properties.

[00117] It is possible to produce different “grades” of polyol products suitable for plastic sheets, rigid foams, flexible foams or expanded “soft” foams by adjusting the ozonolysis and hydrogenation reaction times, ozone flow rate and concentration of the starting vegetable oil.

[00118] For instance, the polyol product produced in Example 5 below is suitable for making hard, brittle plastic sheets and rigid foams.

[00119] To obtain softer grades of polymer one can

- a) Reduce ozonolysis time or/and
- b) Reduce ozone flow rate or/and
- c) Increase the concentration of the starting vegetable oil in the starting solution.

With the current HPLC analysis method and high purity HPLC standards of mono-ol, diol and triol, it is possible to know quantitatively the ratios of each triol, diol and mono-ol fractions. Furthermore the ability to produce different grades of polyol mixtures has been demonstrated in the present application.

[00120] The FTIR spectra of the starting oils and the different polyols are shown in **Figure 18a**. The spectra are dominated by absorptions arising from triacylglycerols, which form the major component of vegetable oils (See, for example, the SDBS-Web library at <http://www.aist.go.jp/RIODB/SDBS>. Accessed April 02, 2005). The absorption bands common to all the samples and present in all spectra are those between 2800 and 3000 cm^{-1} characteristic of saturated C-H stretching modes, the carbonyl absorption band present at 1730 cm^{-1} characteristic of the ester and the absorption triplet (1238, 1166 and 1100 cm^{-1}) characteristic of the triacylglycerol ester. In the small wavenumbers range, the intensity of the sharp 722 cm^{-1} absorption peak representative of the amount of saturated carbon chains (>4C) was reduced by approximately half, clearly revealing a reduction of carbon chains as expected for this procedure. Even in the presence of these strong absorptions, it was possible to see spectral contributions arising from particular functional groups. An absorption band at 3300 cm^{-1} , characteristic of the hydroxyl group, is missing in the spectra of the original canola and flax starting oils, but appears in the spectra of the polyols. The band at 1650 cm^{-1} characteristic of C=C double bond absorption disappears after completion

of the overall reaction indicating a significant loss of double bonds (**Figure 18b**). Other evidence of double bond saturation is the reduction of the small absorption line at 3006 cm^{-1} , indicative of unsaturated C-H stretches, to a very small shoulder of the strong 2925 cm^{-1} absorption peak in the case of air-fed reactions, and complete disappearance for the oxygen-fed reactions (**Figure 18c**). Based on the above, it was confirmed that polyols were produced from vegetable oils by ozonolysis and hydrogenation reactions.

[00121] The hydroxyl and acidity numbers and the refractive indices of the polyols derived from canola and flax oils are shown in **Table 2**. The acidity numbers are similar for canola-air and flax-air polyols whereas the hydroxyl number of canola-based polyols was observed to be higher than that of flax-based polyols. As expected, since more oxygen was readily available to cleave double bonds during the ozonolysis reaction, the polyols obtained with oxygen as a supply gas were observed to have higher hydroxyl and acidity numbers than the polyols obtained with air. The method can produce polyols with relatively lower hydroxyl values than other technologies, because it produces only primary alcohol groups (preferred due to the superior strength they introduce in the polyurethanes) rather than secondary alcohol groups which have the possibility of more than one available position on each carbon chain. Theoretically there is a maximum hydroxyl value of 294 mg KOH/g that can be obtained when producing polyols with 3 primary alcohols from canola and flax oils. The hydroxyl value for the polyol is lower than the theoretical maximum hydroxyl value due to incomplete ozonolysis reactions as well as chemical properties of the starting material. Triacylglycerol oils contain a mixture of saturated and unsaturated fatty acids, which means that single and double hydroxyl groups will be produced since the starting triacylglycerol does not always contain three unsaturated fatty acids. Single and double hydroxyl groups can also be produced if the ozonolysis reaction does not cleave all the double bonds on all the fatty acids. As such, hydroxyl numbers do not provide a good measure of the polyhydroxyl nature of the polyol across various different compounds. However, within a class of compounds (such as within the primary polyols produced by the methods described herein) it can serve as a good comparison measure.

[00122] Nonetheless, the functionality of polyols produced by the methods described herein produce superior polyurethanes, regardless of the lowered hydroxyl numbers.

Table 2: Calculated and experimental amounts in grams of short chain by-product from 100g canola and flax oil. (Errors are standard deviations, n=3).

	Hydroxyl number (mg KOH/g)	Acidity number (mg KOH/g)	Viscosity at 25°C (Pa.s) $\pm 5 \times 10^{-4}$	n_D^{35} $\pm 5 \times 10^{-4}$
Canola oil	3.51 ± 0.18	0	0.0524	1.4670
Canola-air	152.4 ± 0.3	22.9 ± 0.3	0.4527	1.4663
Canola-oxygen	176.4 ± 0.5	51.7 ± 0.1	0.9067	1.4658
Flax oil	5.97 ± 0.41	0.16 ± 0.0	0.0369	1.4760
Flax-air	128.7 ± 2.4	23.1 ± 0.2	0.7970	1.4675

[00123] Evidence that a triply-hydroxylated polyol is produced in the present embodiment is shown in the HPLC chromatograph of the canola-air polyol (**Figure 19**). The appearance of the sharp peak at a retention time around 15 minutes indicates a polyol that contains three carbon chains with primary hydroxyl groups. The first group of peaks centered at the retention time around 4.5 minutes and the second group of peaks centered around 8.5 minutes correlate to the single and double-hydroxyl groups produced during the reaction respectively. Similar phenomena were also observed in the other two polyols produced.

[00124] The DSC melting profiles shown in **Figure 20b** further evidence the suitability of the polyols to processing within standard polyurethane-forming capital equipment present in plants currently. The thermograms of hydrogenated oils which contain the maximum stearic acid amount are also displayed for comparison. The polyols thermograms show some similarities and their crystallization and melting peaks are stronger and more clearly defined than those of the vegetable oils. Clearly, depending on the polyol, various levels of crystallinity are present in the sample at higher temperatures. From the DSC crystallization profiles (**Figure 20a**), the first crystallization peak of the flax-air polyol is shown to be higher than that of the canola-air polyol (19.9 °C for Flax air against 2.3 °C for canola air). **Table 3** summarizes the crystallization temperatures and melting temperatures

(temperatures determined with $\pm 0.5^\circ\text{C}$ uncertainty). Compared to standard values for commercially available polyols, the polyols synthesized were well within acceptable tolerances for standard capital equipment. Presence of crystals can be a barrier to mass transfer of crosslinkers, which can be either a problem or a benefit, depending on what type of polyurethane is being processed. Furthermore, the presence of crystals clearly affect the viscosity of the sample, which results in different requirements on the shear and pumping systems of the plant, etc. However these variances in crystallinity and viscosity can be manipulated well within the plant environment to create polyurethanes with desirable properties.

Table 3: Crystallization and melting temperatures obtained from DSC

	Crystallization			Melting		
	T _{1C} (°C)	T _{2C} (°C)	T _{3C} (°C)	T _{1M} (°C)	T _{2M} (°C)	T _{3M} (°C)
Canola oil	-25.4			-16.6		
Canola-air	-9.6	2.3		-8.7	-0.7	8.21
Canola-oxygen	-25.4	16.8	29.6	-4.5	23.2	39.7
Flax oil	-22.5			-26.6		
Flax-air	-20.1	19.9		-20.4	-5.7	26.3

[00125] Due to hydrogen bonding induced by hydroxyl groups of the polyols, the measured viscosities of the polyols were significantly higher than those of the starting oils, and those with higher hydroxyl numbers demonstrate the highest viscosities. **Figure 21a** shows the viscosity of the samples measured at 25 °C as a function of time indicating Newtonian behavior. The viscosity of the starting oils and the sample polyols decreased with increasing temperature (**Figure 21b**) as expected for such materials. The viscosities of the

flax-based polyol are higher than those of canola-air polyols, despite the fact that the hydroxyl number of the former is relatively lower. This is due to the effect of crystallization on viscosity. Because the first crystallization peak of the flax-air polyol is higher than that of the canola-air polyol, when measurements of viscosity are taken at 25 °C, crystalline structure has already begun to form within the flax-air polyol, attributing to a much greater viscosity. Canola-oxygen polyol displays an even greater viscosity at the same temperature due to its higher hydroxyl value as well as a crystallization peak at 29.6 °C. As expected, this effect dramatically diminishes when the temperature increases, and the gap between the polyols viscosities narrows substantially as seen in **Figure 21b**.

[00126] In yet another embodiment of the present invention, polyols synthesized from agricultural feedstock, such as canola and flax oils, and soybean oil-derived polyols and crude castor oil obtained commercially, and as described herein are reacted with aliphatic diisocyanates and aromatic diisocyanates to produce polyurethane (PU) polymers, further details of which are set out in **Example 4** below.

[00127] The reaction of aliphatic 1,6-hexamethylene diisocyanate (HDI) with polyols synthesized from canola, flax and soybean oils was observed to yield PU elastomers. The reaction of aromatic diphenylmethane diisocyanate (MDI) with polyols synthesized from canola and soybean oils was observed to yield rigid PU foams.

[00128] Such PUs were characterized for their thermal and mechanical properties with dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) as well as tensile and compressive properties measurements. The glass transition temperatures (T_g) of the PU elastomers were found to be lower T_g s (< 0 °C) than those of the PU rigid foams (> 56 °C).

[00129] In the case of the elastomers, the formation of hydrogen bonds is evidenced by FTIR measurements. The TGA thermographs showed clearly two well-defined steps of degradation for all the elastomers. In the first step, up to 30% weight loss, the fastest rate of loss was found at 345 °C for canola-based PU, and at 330 °C for flax-based PU while soy-based PU lost most of the weight in the second step. With the same OH/NCO molar ratio,

the elastomers made from canola-based polyol showed slightly higher Young's modulus and tensile strength than those made from flax-based polyol and soy-based polyols.

[00130] The PU foams produced from canola-based polyols performed better with higher compressive strength and modulus and more uniform cellular structure. The flax-based polyols were not suitable to produce PU foams.

[00131] The FTIR spectra for the three elastomers (designates as COBPU, FOBPU and SOBPU, see Example 4 below) with OH/NCO molar ratio of 1.0 are shown in **Figure 22**. The -NCO group absorption band centered at 2270 cm^{-1} is clearly missing, and a strong 3340 cm^{-1} absorbance band characteristic of the N-H group and an absorbance band characteristic of the C=O group centered around 1700 cm^{-1} are present in all the FTIR spectra. FTIR measurements confirmed that almost all of the diisocyanate groups reacted during polymerization and formed urethane linkages, urea and amide groups.

[00132] The existence of hydrogen bonds, a very important feature of polyurethanes which has significant effect on material properties, was directly observed in the FTIR spectra as seen in **Figure 22**. The band centered around 1700 cm^{-1} split into two resolved branched peaks indicating the presence of hydrogen bonded urethane carbonyl (C=O) groups (Yu, T.L., T.L. Lin, Y.M. Tsai and W.J. Liu, Morphology of polyurethanes with triol monomer crosslinked on hard segments., *J. Polym. Sci.: Polym. Phys.*, 37: 2673-2681 (1999)). Based on the fact that the wave number of the hydrogen bonded urethane C=O group is usually lower than that of non-hydrogen bonded C=O groups (Coleman, M.M., K. H. Lee, D. J. Skrovanek and D. C. Painter, Hydrogen-bonding in polymers. 4. Infrared temperature studies of a simple polyurethane., *Macromolecules*, 19: 2149-2157 (1986)), the position of hydrogen bonded C=O groups was assigned to the 1690 cm^{-1} wavelength, and that of non hydrogen bonded C=O groups to the 1740 cm^{-1} wavelength. The N-H group is another strong proton donor which can forms hydrogen bond as well, but it was not resolved from the FTIR spectra due to its vibration region overlap with the O-H vibration region (around 3300 cm^{-1}).

[00133] For COBPU and FOBPU elastomers, the intensity ratio of hydrogen bonded to non hydrogen bonded peaks was observed to be higher than that of the SOBPU sheet, indicating that more hydrogen bonds were formed for the former two PUs than the latter. Since the

presence of hydrogen bonds would enable the material to dissipate energy without breaking covalent bonds, they are a dominating factor in the resulting mechanical properties which are discussed later.

[00134] The glass transition temperature (T_g) of crosslinked PUs are affected by several factors including the relative amounts of the soft (polyols) and hard (diisocyanate) segments, the cross linking density, and the amount of hydrogen bonding. As expected, T_g s increased with decreasing OH/NCO molar ratio. At Low OH/NCO molar ratio, the PUs exhibit a higher T_g because the excess NCO groups continue to react with the existing urethane groups and form more crosslinked structures. On the other hand, when OH/NCO > 1, the excess OH groups may act as plasticizers and as a result, decrease T_g . This trend is consistent with what has been reported by Petrovic et al (Petrovic, Z.S., W. Zhang, A. Zlatanic, C. C. Lava and M. Ilavsky, Effect of OH/NCO molar ratio on properties of soy-based polyurethane networks., *J. Polym. & Environ.*, 10: 5-12 (2002)).

[00135] **Figure 23** shows an example of the reversing heat flow vs. temperature curves obtained for COBPU and FOBPU with the OH/NCO molar ratio of 1.0. The T_g s were determined from the shift of heat capacity with temperature and the results for the different OH/NCO molar ratios are listed in Table 4. It is obvious that T_g s increased with the decreasing OH/NCO molar ratio for both COBPU and FOBPU elastomers.

[00136] Typical TMA curves of COBPU and FOBPU elastomers are shown in **Figure 24**. TMA analysis evidenced the strong dependence of the PUs thermal behavior on the type of polyol used in their formulation. The T_g s were determined from the intersect of two tangents, one to the low-temperature thermal expansion curve and the other to the thermal-expansion curve beyond the transition following the ASTM E 1545 standard. The deflection observed in the TMA graphs of the FOBPU samples extending from around 0 to 45°C fell in their melting temperature range accounting for the imprecision in the determination of T_g by TMA. The T_g s determined from TMA were lower compared to DMA and MDSC, but the trend was the same: the lowest T_g was recorded for COBPU and the highest was observed for FOBPU. The glass transition determination is not unique

because it is both thermodynamic and kinetic in nature (McKenna, G. S. In *Comprehensive Polymer Science: Vol. 2, Polymer Properties*; Booth C., Price, C., Eds.; Pergamon: Oxford, pp 311-362, 1989) (Table 4)

[00137] **Figure 25** shows the evolution with temperature of the storage moduli (E') of the COBPU, FOBPU, and SOBPU elastomers with OH/NCO molar ratio of 1.0 and illustrates typical dynamic mechanical behavior of our samples. At the same temperature, E' of SOBPU is much lower than those of the other two PUs. A β -transition at approximately -70°C was observed for both COBPU and SOBPU samples, which was not found for FOBPU samples. The T_g of the SOBPU (-43°C) was also lower than that of COBPU and FOBPU samples. This is probably due to a smaller amount of hydrogen bonding in SOBPU compared to COBPU and FOBPU and the presence in SOBPU networks of dangling chains created because of hydroxyl groups located in the middle of the chains. The dangling chains cause significant steric hindrance to further cross-linking, and result in lower cross-linking densities

Table 4 - T_g ($^\circ\text{C}$) of the polyurethane elastomers.

molar ratio (OH/NCO)	Canola oil based PU elastomers			Flax oil based PU elastomers		
	DMA	TMA	MDSC	DMA	TMA	MDSC
1.0:0.8	-11	-26	-20	-8	-12	-8
1.0:1.0	-8	-17	-15	-6	-16	-4
1.0:1.2	-5	-14	-9	-5	-10	-3

[00138] Based on the theory of rubber elasticity (22), the cross-linking density (ν_e) was determined as:

$$E' = 3\nu_e RT \quad (2)$$

where E' is the storage modulus in the rubbery plateau above T_g (ca. $T = T_g + 40^\circ\text{C}$), R is the gas constant.

The values of ν_e obtained for COBPU are 2.3×10^2 , 3.3×10^2 and 4.8×10^2 M/m³, for OH/NCO molar ratios of 1.0:0.8, 1.0:1.0 and 1.0:1.2 respectively, and in the case of FOBPU they are 3.5×10^2 , 5.3×10^2 and 8.3×10^2 M/m³. This indicates that the flexibility of the polymer chains was reduced in the higher cross-linked networks increasing the T_g and thus shifting the rubbery state to higher temperatures.

[00139] The measured glass transition temperature is dependent upon the physical property measured, the type of measuring apparatus and the experimental parameters used. Changes in heat capacity, viscosity, dielectric relaxation, or thermal expansion coefficients used to probe the shift from glassy to rubbery state, could yield very different T_g values (Eisenberg, A. In *Physical Properties of Polymers*; American Chemical Society: Washington, DC, pp 61-96 (1993)). DSC is very sensitive to any additional phenomenon which occurs near the T_g process and its evaluation is affected (Hutchinson, J.M., Characterising the glass transition and relaxation kinetics by conventional and temperature-modulated differential scanning calorimetry., *Thermochimica Acta* 324: 165-174 (1998)). The temperature variation rate has also a direct influence on the heat capacity, especially at T_g , with heat transfer effects complicating the process (Hutchinson, J.M., Studying the glass transition by DSC and TMDSC., *Journal of Thermal Analysis and Calorimetry*, 72: 619-629 (2003)). Standard DSC does often provide only a weak indication of T_g and sometimes does not reveal its existence at all, as our measurements have shown. MDSC, however, minimizes this problem by providing not only the total heat flow signal but also the heat capacity and its kinetic components. The total heat flow is divided into Reversing Heat Flow and Nonreversing Heat Flow. Reversing Heat Flow is the heat capacity component of the total heat flow and is calculated by converting the measured heat capacity into a heat flow signal using the classical heat flow equation as a theoretical basis. As a result, T_g can be determined from the Reversing Heat Flow signal (Wunderlich, B., The tribulations and successes on the road from DSC to TMDSC in the 20th century the prospects for the 21st

century., *Journal of Thermal Analysis and Calorimetry*, 78: 7-31 (2004)). If TMA does not always show a clear glass transition (as shown with the mentioned imprecision in our TMA determination of T_g), it however yields repeatable measurements associated with T_g s (Khandare, P.M.; J.W., Zondlo and A. S., Pavlovic, The measurement of the glass transition temperature of mesophase pitches using a thermomechanical device., *Carbon*, 34: 663-669 (1996)). The DMA provides the most credible information on changes that occur during glass transition and therefore is well-suited to measuring T_g . DMA is very sensitive to the glass transition because the mechanical properties such as modulus and damping, measured by DMA depend strongly on the material's relaxation time which undergoes large changes during the glass transition (Williams, R.J., Methods for Determination of Glass Transitions in Seeds, *Annals of Botany* 74: 525-530, (1994)). The DMA traces are frequency dependent but yield unambiguous peaks for the T_g .

[00140] TGA curves of the PU elastomers with OH/NCO molar ratio of 1.0 and their derivatives (DTGA) are shown in **Figures 26a and 26b** respectively. Decompositions started at approximately 160 °C, losing weight very slightly until 300 °C, where a rapid drop followed and ended at approximately 490 °C. The initial rate loss (for weight loss < 10%) was slightly lower for FOBPU than for COBPU and SOBPU. In the temperature range of 160-300 °C, the shapes of the weight loss curves of all the PUs were similar and in the temperature range of 300-400 °C, totally different. DTGA data (**Figure 26b**) reveal two main degradation processes, one correlated with the first 25-30% of the weight loss, and the second with the remaining weight loss. The shapes of the DTGA curves are practically the same. COBPU had its fastest rate of loss at 345 °C, and FOBPU and SOBPU both had their fastest rate of loss at 330 °C. SOBPU lost most of the weight in the second step, while COBPU and FOBPU both lost around 25% of the weight in the first step.

[00141] The degrading process is complex but it is known that the first stage of degradation is dominated by urethane bond decomposition and that the amount of residue is correlated with the amount of unreacted isocyanate in polymers (Petrovic Z.S., Z. Zavargo, J.H. Flynn, and W.J. Macknight, Thermal-Degradation of Segmented Polyurethanes, *J. Appl. Poly. Sci.*, 51 (6): 1087-1095 (1994)). Javni et al. (Javni, I., Z.S. Petrovic, A. Guo and R. Fuller, Thermal stability of polyurethanes based on vegetable oils., *ibid.* 77: 1723-1734 (2000))

previously reported that although the early stage of degradation is dominated by urethane bonds decomposition, the polyol component may contribute to the weight loss at higher conversions, causing an increase of activation energy. This suggests that the first step of the COBPU and FOBPU losses is likely due to a higher conversion of –NCO groups to urethane bonds compared to that in SOBPU samples and that the difference in the fastest weight loss (330 °C vs. 340 °C) could be linked to differences in the activation energies introduced by the different polyol types.

[00142] Tensile properties were characterized for the PU elastomers. The stress vs. strain curves for the PU sheets with OH/NCO molar ratio 1:1 are shown in **Figure 27**. Similar results were obtained for the other two sets of specimen with different molar ratio and summarized in **Table 5**. Young's modulus and tensile strength at break increased with increasing diisocyanate content, which are well known features in urethanes. With the same OH/NCO molar ratio, COBPU had the highest Young's modulus, tensile strength at break and largest elongation, while SOBPU has the lowest. The higher strength and modulus of COBPU was due to its high hydrogen bonds content and the excessive density of crosslinks which hindered molecular motion.

Table 5. Mechanical properties of polyurethane elastomers at various OH/NCO molar ratios. Errors are standard deviations, n = 5.

	Molar ratio (OH/NCO)	Young's Modulus (MPa)	Strength at break (MPa)	Strain at break (%)
Canola based polyol/HDI	1:0.8	3.08 ± 0.07	1.00 ± 0.05	41.59 ± 3.86
	1:1	4.82 ± 0.15	1.58 ± 0.13	43.05 ± 3.19
	1:1.2	5.71 ± 0.18	2.09 ± 0.17	44.29 ± 3.32
Flax based polyol/HDI	1:0.8	2.76 ± 0.13	0.99 ± 0.08	46.90 ± 3.49
	1:1	4.58 ± 0.17	1.39 ± 0.09	40.54 ± 3.54

	1:1.2	5.83 ± 0.26	1.79 ± 0.10	41.72 ± 1.74
Soybean based polyol/HDI	1:0.8	1.51 ± 0.04	0.29 ± 0.06	26.35 ± 0.79
	1:1	2.80 ± 0.23	0.55 ± 0.04	22.93 ± 2.27
	1:1.2	3.32 ± 0.26	0.63 ± 0.04	22.44 ± 0.59

[00143] The FTIR spectra of Canola-PU, Soybean-PU and Castor-PU foams are shown in **Figure 28**. A broad absorption band at 3340 cm^{-1} characteristic of the hydrogen bonded N-H group and an absorbance band centered around 1720 cm^{-1} characteristic of the C=O group are present in all the FTIR spectra (Szycher, M., *Szycher's Handbook of polyurethanes*, CRC Press, Boca Raton, FL., 1999). However, both bands are not symmetrical. The asymmetrical shape of the band around 1720 cm^{-1} shows that the hydrogen bonded C=O group vibration region is overlapping with the free C=O group vibration region. In the case of N-H wavelength region, a shoulder was observed around $3400 - 3500 \text{ cm}^{-1}$ which is usually assigned to free N-H group, indicating that only part of the N-H group are hydrogen bonded. The decrease of the degree of hydrogen bond formation is due to the steric hindrance effect of the isocyanate aromatic rings and the restriction of hard segment mobility of the chemical crosslinking. In addition, the band centered at 2270 cm^{-1} characteristic of the -NCO group observed in all spectra indicated that the isocyanate has not completely reacted with the polyols. For the same OH/NCO molar ratio, its relative intensity in Soybean-PU and Castor-PU was higher than that in Canola-PU foams. Furthermore, Canola-PU foams had a relatively higher N-H peak than the other two foams. These clear differences, even if precise quantitative analyses of the FTIR results are lacking, shows that the -NCO amount left after the reaction was lower and the urethane linkages amount was higher in the case of Canola-PU foams. It evidences the strong effect of the dangling chains on the reaction and on the degree of its completion. In the case of soybean oil based polyols and crude castor oil, the presence of dangling chains caused significant steric hindrance to crosslinking and resulted in less complete reactions with the isocyanate than that of canola based polyol, and yielded a smaller amount of hard segment in the PU.

[00144] Dynamic mechanical behavior of Canola-PU, Soybean-PU and Castor-PU foams with plots of the storage modulus (E'), loss modulus (E'') and tangent δ ($\tan \delta$) as a function of temperature are shown in **Figure 29a**, **Figure 29b** and **Figure 29c**, respectively. The storage modulus, E' , as highlighted by its first derivative (insert in **Figure 29a**) drops first gradually then exhibits a relatively rapid drop around -90°C and another large drop around 50°C during the transition from glassy to rubbery states. The first rapid drop is attributed to the β – transition and the second to the glass transition. The β – transition may be related to the rotation (Petrovic, Z. S., W. Zhang, and I. Javni, Structure and properties of polyurethane prepared from triacylglycerol polyols by ozonolysis, *Biomacromolecules*, 6: 713-719 (2005)) or backbone chain motion of the short groups (Nielsen, L. E. and R. F. Landel, *Mechanical Properties of Polymers and Composites*, 2nd ed. Marcel Dekker, NY, 1994) in the fatty acid chains. Below T_g , the E' of Castor-PU foams was the highest. Once T_g is reached, the E' begins to decrease rapidly. The E' for Soybean-PU foams decreases at a slower rate and plateaus at a higher level than Canola-PU and Castor-PU foams. In the case of soybean polyol based PU foams, the dangling chains act as a plasticizer which broadens its transition range and reduce its storage modulus. Generally, with the increase of crosslinking density, the transition region broadens, and the modulus drops at a lower rate and plateaus at a higher level. At least part of the broadening of the transition region is due to the heterogeneities in the molecular weight between crosslinks.

[00145] The T_g s listed in **Table 6** were determined with a very good accuracy from **Figure 29a** following ASTM E1640-99 standard.

Table 6: Glass Transition Temperatures and Compressive Properties of PU Foams

	Canola PU	Soybean PU	Castor PU
T_g	58	67	56

Compressive strength (KPa)	770 ± 145	410 ± 50	1170 ± 140
Modulus (MPa)	22.2 ± 7.5	14.4 ± 1.4	30.1 ± 3.4

[00146] Soybean-PU has a higher T_g because it has a higher OH number and hence a higher crosslinking density. Crosslinks hinder the polymer segmental motion by introducing restrictions on the molecule motion of a chain therefore increasing T_g .

[00147] A weak transition at about 0°C was observed for all the PU foams as clearly revealed by the first derivative of E' (arrow in the insert of **Figure 29a**). This weak transition was also observed in the loss modulus curves shown in **Figure 29b**. In the case of Canola-PU, it appeared as a broad shoulder between -50°C to 10°C. Petrovic et al. (Petrovic, Z. S., W. Zhang, and I. Javni, Structure and properties of polyurethane prepared from triacylglycerol polyols by ozonolysis, *Biomacromolecules*, 6: 713-719 (2005)) reported the same phenomena for similar PU systems. In addition, it was found that the two main loss modulus peaks of Soybean-PU foams were much broader than for the other two foams, indicating a broader distribution in crosslinking density. Similar behavior was observed for the $\tan \delta$ curves shown in **Figure 29c**.

[00148] TGA curves and their calculated derivatives (DTGA), shown in **Figure 30a** and **30b** respectively, illustrate the degradation behavior of the PU foams. The decompositions of the PU foams started at higher temperature than in the PU elastomers (approximately 200°C against 160°C). (Narine, S. S., X. Kong, L. Bouzidi and P. Sporns, *Physical Properties of Polyurethanes Produced from Polyols from Seed Oils. I- Elastomer*, Submitted to JAOCS (2006)). The DTGA curves show two separate main features which are associated with two distinct degradation stages. The first feature which ends at around 400°C has well-resolved peaks specific to each structure (3 peaks for Soybean-PU and Castor-PU, and 2 peaks for Canola-PU). The second feature is a relatively broad signal which ends abruptly and is practically the same for all specimens. In the first stage, the fastest rate of loss was at 335°C for Canola-PU, and at 380°C for Soybean-PU and Castor-

PU. The second stage involved an estimated weight loss of 70% with the fastest rate of loss situated at 470°C for all samples.

[00149] The degrading process is complex and depends on several factors such as urethane bonds, polyol type, dangling chains and unreacted isocyanate. The degradation started at a higher temperature than that of the elastomers mainly because the MDI aromatic rings used to prepare the foams affect the activation energy of the formed urethane groups, and delay their dissociation. In the first stage, the similarity of all the samples degradation processes could be explained by similar conversion of $-NCO$ groups to urethane bonds and the differences in the fine structure and shifts of maximum loss rate peaks could be explained by the differences in the activation energies introduced by the dangling chains present in the soybean polyol and castor oil. The second stage where most of the weight loss occurred could be correlated to a similar decomposition process of the polyols backbone.

[00150] The mechanical properties of the foams were characterized by compressive stress-strain measurements and the results are shown in **Figure 31**. After an initial near-linearity of stress to strain up to about 3%, the specimens exhibited relatively abrupt yielding, followed by a sustained plateau region over which there was a little increase in stress with increasing strain. The initial linear region determines the modulus of the foam. The broad plateau region results from a plastic collapse or cell wall buckling of the foams, which is referred to as the collapse stress.

[00151] Young's modulus was calculated according to the ASTM D1621-00 standard. With a density of 160 kg/m^3 , the Canola-PU foam has a compressive strength of $770 \pm 145 \text{ KPa}$ and a modulus of $22.2 \pm 7.5 \text{ MPa}$. The Castor-PU foam yields the highest compressive strength ($1170 \pm 140 \text{ KPa}$) and modulus ($30.1 \pm 3.4 \text{ MPa}$). With the same density, the modulus and compressive strength of the Soybean-PU foam are substantially lower ($14.4 \pm 1.4 \text{ MPa}$ and $415 \pm 50 \text{ KPa}$ respectively).

[00152] The compressive strength and modulus depend primarily on the cellular structure of the foam, i.e. the material of the cell walls and the size and shape of the cells. The lowest compressive strength of soybean-PU samples is the result of the plasticizing effect of the dangling chains combined with a smaller amount of hard segments. The plasticizer weakens the network under load and lowers the compressive strength and Young's

modulus. The hard segments confer to the PU foams high modulus, especially when they are of non-uniform size and therefore more difficult to disrupt. The high compressive strength and modulus of castor-PU foams is mainly due to the size and shape of the cells and the thickness of the cell walls and will be discussed later.

[00153] The cross-sectional surfaces of the foams observed with SEM are shown in **Figure 32**. Canola-PU foams have small pores of approximately 0.25-mm diameter, uniformly distributed with relatively thin walls (**Figure 32a**). Soybean-PU foams have a less uniform structure composed of larger elongated strips-like pores interconnected by smaller pores of different sizes (**Figure 32b**). In the case of Castor-PU foams, the cells are very coarse even observed by naked eye and have the largest wall width (**Figure 32c**) which resulted in the highest compressive strength and modulus. The relatively poor quality of the Castor-PU foam microstructure might be attributed to its inadequate optimization of the surfactant used in its formulation. It is known (Szycher, M., *Szycher's Handbook of polyurethanes*, CRC Press, Boca Raton, FL., 1999) that the role of the surfactant is to stabilize the cell walls by lowering the surface tension between the cells and prevent their coalescence, resulting in smaller cells uniformly distributed over the network. Meanwhile, catalysts are added to accelerate reactions according to the requirement. The final cellular structure is a balance between the network formation and the blowing reaction. In the case of Castor-PU foams, when the amounts of catalysts are reduced to 0.5 parts, finer cells with narrow distribution were obtained.

[00154] In yet another embodiment of the present invention, polyols synthesized *via* modified ozonolysis and hydrogenation methods from agricultural feedstock (which are set out in **Example 5** below), such as canola oil-derived polyols, and as described herein are reacted with aromatic diisocyanates to produce polyurethane (PU) polymers, such as rigid foams.

[00155] The HPLC was performed on the products from the modified ozonolysis and hydrogenation method. HPLC of polyols produced with Pd-C, Raney Ni System and HPLC of polyols produced with Zinc, Raney Nickel System are shown in **Figure 33** and **Figure 34** respectively. It can be seen that with the new method in both procedures, the peak of mono-

ol which is a chain terminator in the cross linking has disappeared, the saturated fat peak was very small and that the peak of triol is much bigger compared to diol peak

[00156] Using the recycled ethyl acetate as the solvent for the new ozonolysis method with Pd-C, Raney Ni System as the catalyst for hydrogenation, polyols with a large amount of triol and almost free of mono-ol were also produced. **Figure 35** shows the HPLC performed on these polyols and qualitatively verify their quality.

[00157] **Figure 36a** shows the viscosity of the polyols measured at 35 °C as a function of time indicating Newtonian behavior. The viscosity of the starting oils and the sample polyols decreased with increasing temperature (**Figure 36b**) as expected for such materials. The viscosities of the canola oil based polyol synthesized using ethyl acetate are higher than those of canola oil based polyol synthesized using recycled ethyl acetate.

[00158] Such PUs were characterized for their thermal and mechanical properties with dynamic mechanical analysis (DMA), as well as compressive property measurements.

[00159] Dynamic mechanical behavior of Ethyl Acetate Canola Oil Based PU (EACOBPU) and Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU) foams, with plots of the storage modulus (E'), loss modulus (E'') and tangent δ ($\tan \delta$) as a function of temperature are shown in **Figure 37a**, **Figure 37b** and **Figure 37c**, respectively. The T_g of the Ethyl Acetate Canola Oil Based PU (EACOBPU) and Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU) foams were 50 and 51°C, respectively.

[00160] The mechanical properties of the foams were characterized by compressive stress-strain measurements and the results are shown in **Figure 38**. Young's modulus was calculated according to the ASTM D1621-00 standard. With a density of 160 kg/m³, the EACOBPU foam has a compressive strength of 1028 ± 126 KPa and a modulus of 23.3 ± 6.6 MPa. The REACOBPU foam yields the highest compressive strength (812 ± 110 KPa) and modulus (15.5 ± 3.1 MPa).

[00161] Embodiments of the invention are described by reference to the following specific examples which are not to be construed as limiting.

Examples

Materials

[00162] Triolein (minimum 95% purity) and the Raney nickel 2800 (slurry in water) catalyst were obtained from Sigma-Aldrich Co. Tristearin was obtained from Applied Science Laboratories. Pentane, glacial acetic acid, ethyl ether, anhydrous sodium sulfate, Celite, dichloromethane (HPLC grade), heptane (HPLC grade), 2-propanol (isopropanol, HPLC grade), ethyl acetate and hexane were all obtained from Fisher. Tetrahydrofuran was obtained from Caledon and certified grade Tetrahydrofuran (THF) was purchased from Fisher Scientific, USA. Elemental zinc powder was obtained from Merck. Silica gel (230-400 mesh) was obtained from Rose Scientific Ltd, Alberta. Si-Diol Silica Gel (230-400 mesh) and the aluminum backed TLC plates (250 μ m thickness) were obtained from Silicycle Chemistry Division, Quebec. All chemicals were reagent grade or better.

[00163] The canola vegetable oil used in this study was from a sample of "100% Pure Canola" supplied by Canbra Foods Limited, Lethbridge, Alberta, Canada and the flax vegetable oil was a sample of "Superb Flax Oil" supplied by Archer Daniels Midlands. Their main fatty acid profiles (Firestone, D., Editor, in *Physical and Chemical Characteristics of Oils, Fats, and Waxes*, AOCS press, Washington, D.C., 1999) are displayed in **Table 7**. Canola and flax oils are predominantly constituted of more than 90% of unsaturated fatty acids. Canola oil contains about 60% oleic acid, whereas flax oil contains over 50% of the more unsaturated linolenic acid.

Table 7: Fatty acid composition of canola and flax oil in weight %.

Fatty acid	Canola (wt %)	Flax (wt %)
Oleic (C18:1 n9c)	56.11	18.88
Linoleic (C18:2 cc)	21.01	16.10

Linolenic (C18:3 n3c)	7.89	53.73
Palmitic (C16:0)	4.09	5.48
Stearic (C18:0)	1.86	3.52

[00164] The gases used for the reactions were 99.5% Extra Dry Grade 2.6 oxygen gas and 99.995% pre-purified Grade 4.5 hydrogen gas, both from Praxair.

Example 1: Preparation of Polyols from Triolein

Step A - Ozonolysis

[00165] Triolein (15g) was dissolved in 150 mL of pentane and brought to -10 °C in a 500 mL three-necked flask using an external 50:50 mixture of glycol water from a Jeiotech VTRC-620 temperature bath from Rose Scientific. Ozone was produced in an Azcozon ozone generator Model number RMV16-16 from Azco Industries Ltd. In an attempt to minimize acid production the ozone treatments (10 min of air flow) were alternated with a nitrogen purge (5 min) at a gas flow rate of 5 L/min. These alternate gas flows were carried out seven times with the final nitrogen purge taking 20 min. The total ozonolysis time was therefore 70 min and the total nitrogen purging 50 min. During the gas flow pentane evaporated so it became necessary to continually top up the solvent level. In total, an additional 350 mL of pentane was required over the entire ozonolysis. The additional pentane was all added prior to the final nitrogen purge when the solution was allowed to warm to room temperature to remove any remaining ozone.

[00166] The remaining residue was quenched with 18 mL of glacial acetic acid and 6.65 g of zinc in the presence of constant agitation using a stir bar over a period of 10 minutes. During this addition the temperature was maintained lower than 30 °C with an ice bath and after 40 min the reaction mixture was dissolved in ethyl ether (150 mL). The ether layer was washed twice with 70 mL of deionized water and the remaining organic layer dried over anhydrous sodium sulfate. Finally the solvent was removed on a flash evaporator (Heidolph Laborota 4001) to yield 15.7 g of a viscous yellow oil.

Step B - Hydrogenation

[00167] The yellow oil from the ozonolysis step (15.7 g) was dissolved in 250 mL of tetrahydrofuran and 1.6 g of nickel catalyst added into a 2L Parr Instrument Co hydrogenation vessel fitted with a magnetic drive. This mixture was flushed 3 times (10 min for each) with nitrogen at 200 psi pressure. The reactor vessel was charged with hydrogen gas at 460 psi at room temperature and the temperature was increased over 15 min to 92 °C with a concomitant increase in pressure to 597 psi. The hydrogenation reaction was carried out at this temperature for 2 h and 10 min and then the temperature was reduced to room temperature with cooling water and a final pressure of 455 psi. The hydrogen was purged from the hydrogenation vessel with nitrogen gas. The remaining mixture was filtered over Celite and (about 3 mL) aqueous layer removed in a separatory funnel. The organic layer was concentrated on a flash evaporator.

[00168] To insure complete hydrogenation the above procedure was repeated. The remaining material was dissolved in 300 mL of tetrahydrofuran with 2.4 g of nickel catalyst added. After flushing with nitrogen the reactor vessel was charged with 410 psi of hydrogen and the temperature increased to 120 °C. This reaction was carried out for 4 h and 15 min followed by a reduction in temperature (final psi of 408); flushed with nitrogen; filtered; water removed, and the remaining organic layer concentrated on a flash evaporator to a light yellow oil (11.4 g).

Step C - Column Chromatography

[00169] A column of dimensions 1.3 id x 30 cm was packed with 11.02 g (about 17 mL volume) of Si-Diol silica gel. Material from the second hydrogenation (0.65 g) was dissolved in 7 mL of dichloromethane and 2 g of the Si-Diol silica gel added. The solvent was then removed with a flash evaporator and this material poured on top of the silica column. The column was then eluted with 50 mL heptane; 50 mL heptane containing 4 % (v/v) isopropyl alcohol (IPA); 50 mL of heptane containing 8% IPA; 200 mL of heptane containing 12 % IPA and finally, 100 mL of heptane containing 16% IPA. The column required about 14 mL of heptane to completely wet it. The fractions were collected as follows 1-19 (5 mL fractions; 20-43 (3 mL fractions) and 44-92 (5 mL fractions).

[00170] The presence of material was confirmed in fractions by thin layer chromatography (TLC) on silica gel plates using a solvent system of 10 % ethyl acetate and 90 % hexane (v/v). Spots were visualized using a 5% sulfuric acid in methanol dip followed by charring with a heat gun. On the basis of TLC and HPLC analysis fraction 76 was isolated and evaporated for further spectroscopic analysis.

Step D - HPLC System

[00171] The HPLC system developed was a modification of the procedure used by Elfman-Borjesson and Harrod (6 Elfman-Borjesson, I. and M. Harrod, Analysis of Non-Polar Lipids by HPLC on a Diol Column. *J. High Resol. Chromatogr.* 20: 516-518 (1997)) for analysis of lipid derivatives. The HPLC system consisted of a dual Milton Roy pump with a 20 μ L auto-injector. The column was a Betasil Diol-100 (5 μ m particle size) 250 x 4 mm produced by Thermo Hypersil-Keystone and maintained at 50 °C with a Biorad column heater. The detector was a Sedex SS SEDERE evaporative light scattering system maintained at 100 °C with a gain setting of 10 (on the 12 unit scale) and a nitrogen pressure of 2 bar.

[00172] A run consisted of a linear gradient of 100% heptane to 1:1 heptane, isopropyl alcohol in 30 min.; then back to 100% heptane in 10 minutes at a flow rate of 3 ml/min.

Step E - NMR and Mass Spectrometry

[00173] *Spectral Data for Fraction 76.* ^1H NMR (CDCl_3) δ 5.27 (m, 1H), 4.30 (m, 2H), 4.16 (m, 2.5H), 4.05 (t, 1H), 3.65 (t, 5H), 2.30 (m, 7.5H), 2.03 (s, 4H), 1.60 (br m, 13.5H), 1.35 (br s, 28.5H). ESI (mass spectroscopy arbitrary ion intensity in brackets) m/z 583.4 (100%); 561.4 (60%), 739.6 (11%), 427.3 (9%), 717.6 (4%). Accurate mass spectroscopy m/z found 561.39933. Calculated for $\text{C}_{30}\text{H}_{57}\text{O}_9$ (protonated "triol") 561.39971. [*NMR for Tristearin.* ^1H NMR (CDCl_3) δ 5.27 (m, 1H), 4.29 (m, 2H), 4.15 (m, 2H), 2.31 (m, 6H), 1.62 (m, 6H), 1.35 (br s, 84H), 0.95 (t, 9H)].

Example 2: Preparation of Polyols from Canola Oil

Ozonolysis Reactor

[00174] The reactor **10** presently disclosed offers an improvement over prior art ozonolysis vessels, such as those utilized by Lin, S. H. and Wang, C. H. (Industrial wastewater treatment in a new gas-induced ozone reactor, *Journal of Hazardous Materials*, **98** 295-309, (2003)) illustrated in **Figure 41** (Prior Art). The reactor of the present invention is fed with a motor **28**, such as a Direct Current Permanent Magnet 1 HP Motor from Leeson electric-corporation, USA. The water, which temperature is controlled by a chiller, is rushed into the outer layer **14** of the reactor (entry labelled “H₂O in”; **16**), circulated around the reaction vessel **12** and evacuated (labelled “H₂O out”; **18**). The water is kept flowing during the reaction to keep the reaction system at a constant temperature. Ozone is generated in an ozone generator (such as Azcozon Model RMV16-16 from Azco Industries Ltd, Canada) with oxygen or air as the feed gas, and introduced into the reactor from the two apertures for ozone input at opposing ends of an ozone inlet channel **24** (the apertures being labelled as “O₃, O₂ in” (**20**) and “O₃, air in” (**22**) in **Figure 39**). The ozone inlet channel **24** is disposed at the lower end of the reaction vessel **12** and extends across the diameter thereof. The gas is released from the ozone inlet channel **24** into the reaction vessel **12** through a plurality of pores **26**, which are evenly spaced across the length of the ozone inlet channel **24**. The non-return valves **36** prevent backflow of the reaction solution to the two apertures for ozone input (**20**, **22**) and the aperture for nitrogen input, **38**.

[00175] The two apertures for ozone input, **20** and **22**, and the pores **26** in the ozone inlet channel **24**, provide for uniform distribution of ozone in the reaction vessel **12**. This improved distribution of ozone increases the effectiveness of the ozonolysis reaction, allowing for shorter reaction times, lowered reaction temperatures, and increased homogeneity of end products. This arrangement differs from prior art ozonolysis vessels, such as the embodiment illustrated in **Figure 41**, which only have a single aperture for ozone input.

[00176] The magnet motor **28** is connected to a longitudinally disposed agitator **30** which extends into the reaction vessel **12**. The motor **28** is kept rotating at high speed during the reaction. The agitator **30** comprises a plurality of pitched blades **32**, which may be fixedly mounted or releasably mounted to the agitator **30** by means known to those skilled in the

art. In one embodiment, the blades 32 may be welded to the agitator 30. In one embodiment, the blades 32 are trapezoidal in shape, which reduces the resistance. In another embodiment, the blades 32 are attached to the agitator 30 at an angle of from about 30 degrees to about 60 degrees. Such an angle of attachment has been found to reduce vortex formation and increase the rate of reaction. In yet another embodiment, the blades 32 contain a plurality of holes 34, which increase contact areas between the reagents and further reduce vortex formation. **Figures 40(a) and 40(b)** illustrate the blades 32 in greater detail in accordance with one embodiment of the invention.

[00177] Thus, in the reactor vessel of the current invention, the apertures for ozone input 20 and 22, the ozone inlet channel 24, the pores 26 within the ozone inlet channel 24, as well as the rotating blades 32 have been designed to ensure thorough contact and full reaction of ozone with the starting material.

[00178] In one embodiment, the blades 32, agitator 30, and reaction vessel 12 may be made of stainless steel, such as SS 316 L.

[00179] In one embodiment of the present invention, the reactor has the following characteristics, which are presently described by way of example and should not be interpreted as limiting. It has been found that a reaction vessel 12 having a volume of 1727 cm³ (diameter = 10 cm; height = 22 cm) can accommodate 200 g of starting material (vegetable oil) in 1000 mL of solvent. The ozone inlet channel 24 comprises twelve pores 26 evenly spaced at 0.8 cm apart, wherein the pores have a diameter of 0.8 mm. The agitator 30 has six blades 32 having the dimensions illustrated in the embodiment shown in **Figure 40(a)**, and the blades 32 contain six holes 34 having a diameter of 0.3 cm. The angle of attachment of the blades 32 to the agitator 30 can vary from about 30 degrees to about 60 degrees. The blades 32, agitator 30, and reaction vessel 12 are made of SS 316 L.

Step A - Ozonolysis

[00180] Canola oil (100g) and deionized water (400g) were poured into a specially designed reactor (schematic shown in **Figure 39** and described above). The reaction was performed at 27°C, at 5 L/min O₂ flow rate and 80 rpm agitation rate. After 5 hours, the ozone

generator was stopped and the reaction vessel was purged with N₂ for 10 minutes to remove the unreacted ozone from the vessel. 400ml of tetrahydrofuran (THF) was then added into the vessel to dissolve the ozonide product. The product was then transferred to a separatory funnel where the organic part was collected for the hydrogenation step.

Step B - Hydrogenation

[00181] 10.5 g of Raney nickel catalyst were added to the ozonide (490.8g) in THF in a hydrogenation vessel (2L, Parr Instrument Co, USA) fitted with a magnetic drive. The reaction vessel was flushed 3 times with nitrogen at 200 psi pressure to remove the air and then was charged with hydrogen gas at 350 psi at room temperature. The temperature was increased over 30 minutes to 135°C with a concomitant increase in pressure to 520 psi. The hydrogenation reaction was carried for 5 hours at this temperature and the pressure decreased with the consuming of hydrogen. The temperature was then reduced to room temperature with cooling water and to a final pressure of 290 psi. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The remaining mixture was filtered over Celite and the aqueous layer removed in a separatory funnel

[00182] To insure complete hydrogenation of the double bonds and ozonolysis products, the above procedure was repeated on the remaining organic material from the separatory funnel. The final hydrogenation product was kept for distillation.

Step C - Gas Chromatography (GC)

[00183] To determine the amounts of short chain compounds present as by-products from the hydrogenation reaction, a Varian 3500 Capillary Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID), a Varian 8200 Auto Sampler and a BP20025 column (30-m long, 0.25-mm internal diameter, and 0.25- μ m thick silica wall) was used. The system was controlled with Varian's "Star Chromatography Workstation" software V.5.51. The injector and the detector temperature were fixed at 250°C. The temperature of the column initially set at 50°C was increased to 250°C in two successive steps: from 50°C to 90°C at a rate of 25°C/minute and from 90°C to 250°C at a rate of 10°C/minute.

Step D - Wiped- blade Molecular Distillation

[00184] The solvent was removed on a rotary evaporator (Heidolph Laborota 4001, UK) to yield a viscous yellow oil. GC analysis showed that the removed THF was 100% pure and no product was also removed with THF. The wiped blade molecular distillation unit (Model VKL 70/ICL-04, from Incon Processing) was set up at a jacket temperature of 115°C, and the temperature of the condenser 30°C. The pressure of the distillation system was reduced to 20 mTorr and the viscous oily product added into the distillation system through an addition funnel at a speed of 1mL/min. After all the product had been added to the distillation system, the unit was kept running for 30 minutes, to allow the complete collection of the residue and distillate. Finally, distillate (31.1g) and residue (47.0g) were obtained. The distillate fractions from the flash evaporator and distillation were analyzed by GC, and the residue fraction analyzed by HPLC.

Step E - Flash Chromatography

[00185] A column of dimensions 3 id × 30cm was packed with 400g (about 212 mL volume) of silica gel (230-400 mesh). Material from the residue fraction of distillation (4.3g) was added. The column was then eluted under air pressure with gradient flow phase composed of hexane and ethyl acetate. The ratios (v/v) of hexane to ethyl acetate was started with 50:1, then gradually decreased to 20:1, 17:1, 10:1, 8:1, 5:1, 3:1, 2:1, 1:1, followed by 1:2, 1:3, 1:4. Finally pure ethyl acetate was used and the fractions were collected in 30mL-test tubes. Ratios of flow phase of 20:1, 8:1, 2:1 and 1:4 were used on fractions 28-50, 131-143, 264-289, and 366-389 respectively. Thin layer chromatography (TLC) was run on each fraction using hexane and ethyl acetate as the developing system with ratios (v/v) of hexane and ethyl acetate of 3:1, 2:1, and 1:1. The glycerides and related compounds were detected by spraying the plates first with methanol containing 10% sulphuric acid (concentration 98%) and then heating them at 200°C for 5 minutes.

Step F - High Performance Liquid Chromatography (HPLC)

The HPLC analysis protocol used was a modification of the procedure developed by Elfman-Borjesson and Harrod (Elfman-Borjesson, I. and M. Harrod, Analysis of Non-Polar Lipids by HPLC on a Diol Column. *J. High Resol. Chromatogr.* 20: 516-518 (1997)) for analysis of lipid derivatives. The HPLC system consisted of a dual Milton Roy pump with a 20 µL auto-injector. The column was packed by Betasil Diol-100 (5 µm particle size) 250×4 mm produced by

Thermo Hypersi-Keytone and maintained at 50°C with a Biorad column heater. The detector was an Alltech EDSL 2000 evaporative light scattering system maintained at 100°C with a gain setting of 10 (on the 12 unit scale) and a nitrogen pressure of 2 bar. Two solvents were connected to the pump as the mobile phase. A is 100% heptane and B 50% heptane with 50% isopropyl alcohol (IPA). A run consisted of a linear gradient of 100% A to 83% A and 17% B in 30 min; then back to 100% A in 1 minute at a flow rate of 3 mL/min.

Example 3: Preparation of Polyols from Canola Oil and Flax Oil

[00186] Three grades of polyols were synthesized in this example: (i) polyols from canola oil using oxygen gas supply to generate the ozone, and referred to as canola-oxygen; (ii) polyols from canola oil using air supply to generate the ozone, and referred to as canola-air; and (iii) polyols from flax oil using air supply to generate the ozone, and referred to as flax-air.

Step A - Ozonolysis

[00187] The preparation of polyols from canola and flax was generally conducted as set out in the previous examples above. Briefly, the polyols were synthesized by ozonolysis of the vegetable oils followed by hydrogenation in the presence of a nickel catalyst. The ozonolysis was carried out in a reactor fed with ozone gas generated by a Model-RMU 16-16 generator from Azco Industries Ltd supplied either with air or oxygen. The hydrogenation was completed in a Parr-Pressure Reaction Apparatus (Parr Instrument Company Inc). The vessel temperature of the hydrogenator is controlled by a 4835-Parr controller. The distillation was carried out in a Model VKL 70/ICL-04 wipe-blade molecular distillation system from Incon Processing. The procedure was as follows: 100 g of triacylglycerol oil was mixed with 400 ml of de-ionized water in a high speed mixer and the mixture sonicated for 1 hr in a Sonic 300-Dismembrator sonicator at full power. The resulting solution was agitated at 500 rpm in the ozonolysis reactor vessel until the temperature of the vessel stabilizes at 0 °C. This step took about 45 minutes to complete. The ozone generator was then supplied with air or oxygen at a constant flow rate of 5 L/min. The ozonolysis reaction was started by directly introducing the generated ozone gas

in the reactor with the solution still agitated at 500 rpm. After about 8 hours, the water was removed and THF (or another suitable solvent) is added. The resulting solution was then transferred to the hydrogenation reactor where the reaction is carried out at 130 °C under pressure of 600 psi for about 8 hours. After the removal of the catalyst and the solvent, the hydrogenated crude was transferred to a wiped blade molecular distillation system to remove the short-chain by-products – i.e. the products were separated into a light fraction and a heavy fraction (polyols).

Step B - FTIR

[00188] The spectra were collected on a Nicolet Magna 750 spectrometer system, equipped with a room temperature MCT-B detector. The liquid samples were analyzed neat as a thin film between two KBr plates. The thickness of the film was manually adjusted to ensure that no peak absorbance was over 1.0 absorbance units. The spectra were recorded in the range 400-4000 cm^{-1} with a nominal resolution of 4 cm^{-1} . A background spectrum of the clean, dry plates was first collected before each absorbance spectrum and 32 interferograms were co-added before Fourier transformation using Nicolet Omnic software.

Step C -GC

[00189] To determine the amounts of short chain compounds present as by-products of the ozonolysis and hydrogenation reactions, a Varian 3500 Capillary Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID), a Varian 8200 Auto Sampler and a BP20025 column (30-m long, 0.25-mm internal diameter, and 0.25- μm thick silica wall) was used. The system was controlled with the Varian “Star Chromatography Workstation” software V.5.51. The injector and the detector temperature were fixed at 250 °C. The temperature of the column initially set at 50 °C was increased to 250 °C in two successive steps: from 50 °C to 90 °C at a rate of 25 °C/minute and from 90 °C to 250 °C at a rate of 10 °C/minute.

Step D - HPLC

[00190] The molecular profile of the polyol products were obtained with a HPLC system using a modified procedure by Elfman-Borjesson and Harrod (11) for analysis of lipid derivatives. The HPLC system consisted of a dual Milton Roy pump with a 20 μL auto-

injector. The column was a Betasil Diol-100 (5 μm particle size) 250 x 4 mm produced by Thermo Hypersil-Keystone and maintained at 50 °C with a Biorad column heater. The detector was an Alltech EDSL 2000 evaporative light scattering system maintained at 100 °C with a gain setting of 10 (on the 12 unit scale) and a nitrogen pressure of 2 bar. Two solvents reservoirs were connected to the pump as the mobile phase. Solvent A was 100% heptane and solvent B was 50% heptane with 50% isopropyl alcohol. A run consisted of a linear gradient of 100% A to 83% A and 17% B in 30 min.; then back to 100% A in 1 minutes at a flow rate of 2 mL/min.

Step E – Rheometric Measurements

[00191] The viscosities of the polyol samples were measured in shearing mode with the Universal Dynamic Rheometer PHYSICA UDS 200 (Paar Physica USA) with a constant shearing rate of 51.6 s^{-1} . The viscosities were recorded at 6 different temperatures, from 50 °C to 25 °C every 5 °C. The viscosities were also measured at 25 °C as a function of time.

Step F – DSC

[00192] The “TA 2920 Modulated DSC” system from TA Instruments was used to study the thermal transitions of the polyols. The data sampling and temperature control procedures were fully automated and controlled by the “TA Instrument Control” software program and the data were analyzed using the “TA Universal Analysis” software. The procedure to record the crystallization and melting curves was as follows: Initially the sample was kept at 20 °C for 5 minutes to reach steady state and then was heated to 80 °C with a rate of 5 °C/min to erase its thermal history. To record the crystallization curve, the sample was cooled down to -50 °C at a constant rate of 5 °C/min and kept at this temperature for 5 minutes to allow the completion of the crystallization. The sample was then heated to 80 °C at a constant rate of 5 °C/min to record the melting curve.

Step G – Refractometry

[00193] The refractive index of the materials was determined according to the ASTM method D1747– 99, with a CARL Zeiss (Germany) refractometer.

Step H - Hydroxyl and acidity values

[00194] The hydroxyl numbers of the polyols were determined according to the ASTM titration method D1957-86 and the acidity values were determined according to the ASTM method D4662-98. Triplicate specimens were measured for each polyol and the average values and standard deviations are reported here.

Example 4: Polyurethane Produced from Polyols from Seed Oils

[00195] In this example, properties of PU elastomers and rigid foams prepared by reacting polyols synthesized from vegetable oils (canola, flax and soybean oils) and crude castor oil and two different classes of diisocyanate (aliphatic and aromatic diisocyanates) are described. Using dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques, their physical and thermal properties were studied and compared and the effect of the dangling chains assessed.

[00196] The canola and flax oil based polyols were synthesized as described above. Soybean-based polyols with hydroxyl groups located in the middle of the fatty acid chains, were sourced from Urethane Soy Systems Company, IL. (USA). Soybean-based polyols with two hydroxyl functional groups were used to produce elastomers and soybean-based polyols with three hydroxyl functional groups were used to produce foams. Castor crude oil was obtained from CasChem Company, NJ (USA). The aliphatic 1,6-hexamethylene diisocyanate (HDI, Desmodur N-3200) and the aromatic diphenylmethane diisocyanate (MDI, Mondur MRS) were sourced from Bayer Corporation, Pittsburgh, PA, USA. The relevant parameters of the polyols and diisocyanates are listed in **Table 8**.

Table 8. The parameters of the used polyols and diisocyanate. Errors are standard deviations, n=3.

	Equivalent weight (g/mole)	OH number (mg KOH/g)	Acidity number (mg KOH/g)

Canola based polyol	368	152.4 ± 0.3	22.9 ± 0.3
Flax based polyol	436	128.7 ± 2.4	23.1 ± 0.2
Soybean based polyol 1*	902	62.2 ± 2.7	7.7 ± 0
Soybean based polyol 2**	302	185.5 ± 3.0	7.6 ± 0.4
Castor oil	340	165.2 ± 3.8	1.8 ± 0.1
HDI	183		
MDI	133		

* Soybean based polyol with two hydroxyl functional groups.

** Soybean based polyol with three hydroxyl functional groups.

Step B - Preparation of the Polyurethanes

[00197] The polyols were used to produce PU elastomers and PU foam samples. They are referred to as Canola Oil Based PU (COBPU), Flax Oil Based PU (FOBPU) and Soybean Oil Based PU (SOBPU) elastomers or Canola-PU, Castor-PU and Soybean-PU foams, respectively.

[00198] To prepare the elastomers, three formulations were used by fixing the molar ratio of the OH to the isocyanate (NCO) group to 1:0.8, 1:1.1 and 1:1.2 respectively. The weights of polyol and isocyanate were calculated on the basis of their respective known equivalent weights (the equivalent weight of polyol (EW_{polyol}) = $56110/\text{OH number}$ in g/mole, the equivalent weight of the isocyanate ($EW_{\text{isocyanate}}$) is provided by the company (183 g/mole for HDI, and 133 g/mole for MDI). Given the total weight of PU (W_{PU}) to produce and the desired OH/NCO molar ratio (M_{ratio}), the weight of polyol (W_{polyol}) needed satisfy the equation below:

$$M_{ratio} = \frac{W_{polyol} / EW_{polyol}}{(W_{PU} - W_{Polyol}) / EW_{Isocyanate}}$$

[00199] A suitable amount of polyols mixture and HDI were weighed in a plastic container, stirred slowly for 5 min, poured in a metallic mould previously greased with silicone release agent, and placed in a vacuum oven at 45 °C for 10 to 20 min to evacuate the CO₂ released during the side reaction. After this time, the sample was solid, but tacky and not fully cured. Air was then introduced to the oven and the sample post-cured for about 48 hours at 40 - 45 °C.

[00200] The formulation to prepare the foams was chosen so that the final hydroxyl number lay between 450 to 500 mg KOH/g in order to obtain the desirable rigidity ((Guo, A., I. Javni, and Z. Petrovic, Rigid polyurethane foams based on soybean oil, *Journal of Applied Polymer Science*, 77: 467-473 (2000)). A typical foam formulation is shown in **Table 9**

Table 9 - Typical foam formulation

Polyol	100.0 part
Glycerin	12.0 – 15.0
Water	2.0 - 3.0
Surfactant	2.0
DBTDL T-12	1.0
DABCO DMEA	1.0
Crude MDI Index	1.2

[00201] The polyols were reacted with MDI, in the presence of Dibutyl Dilaurate (DBTDL) from Aldrich Chemical (USA) as the main catalyst, N, N- Dimethylethanolamine (DMEA) from Aldrich Chemical (USA) as the co-catalyst, and glycerin from Fisher Chemicals (USA) as cross-linker agents and distilled water as blowing agent. The surfactant was B-8404 from Goldschmidt Chemical Canada. The specific polyol was first mixed (2 minutes) in a plastic container with suitable amounts of crosslinkers, catalyst, and surfactant. MDI was added and the mixture was stirred vigorously for 40 seconds in the case of Canola and Castor oil based PU foams and for 90 seconds in the case of Soybean oil based PU foams. The mixture was then poured into a home-made TEFLON mould which was greased with the silicon release agent and sealed with a hand-tightened clamp. After the reaction had been completed, the sample was post cured at room temperature for 4 days. Flax based polyols were found not suitable to produce usable foams. Without being bound by theory, it may be that this is due to a very low amount of triol in the flax-based polyol combined with a relatively high amount of saturated fatty acids.

[00202] For the compressive property measurements, foams samples were prepared in circular cylindrical TEFLON molds of 60-mm diameter and 36-mm long. For DMA measurements, rectangular samples were prepared with the same procedure by polymerizing the reactants in (18×13×4 mm)-TEFLON molds.

Step C – FTIR

[00203] The FTIR spectra were recorded on a Nicolet Magna 750 FTIR, equipped with an MCT-A detector and a Nicolet Nic-Plan IR microscope used in transmission mode. The spectra were recorded in the range 650-4000 cm^{-1} with a nominal resolution of 4 cm^{-1} . A background spectrum was first collected before each absorbance spectrum. 128 interferograms were coadded before Fourier transformation using the Nicolet Omnic software.

Step D – Thermal Properties

[00204] DSC measurements were carried out on a TA Instruments MDSC Q100, equipped with a refrigerated cooling system. All the DSC measurements were performed following the ASTM E1356-03 standard. The samples were heated at a rate of 10°C/min from –90°C to +100°C, under a dry nitrogen gas atmosphere. MDSC measurements were performed with a modulation amplitude of 0.5°C and a modulation period of 60 s at a rate of 2°C/min for COBPU and with a modulation amplitude of 0.1°C and a modulation period of 20 s at a rate of 1°C/min for FOBPU and SOBPU.

[00205] DMA measurements were carried out on a TA Instrument DMA Q800 equipped with a liquid nitrogen cooling apparatus, in the single cantilever mode, with a constant heating rate of 1°C/minute from –120°C to +50°C in the case of PU elastomers, and a constant heating rate of 2°C/minute from –120°C to +150°C in the case of PU foams. The measurements were performed following ASTM E1640-99 standard at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.015 mm.

[00206] A TA Instruments TMA (2940) was used to measure the change in dimensions of the PU elastomer while the material was subjected to a constant heating rate of 5 °C/min through the glass transition from –120 °C to +150 °C. The measurements were performed according to ASTM E1545–00 standard. The probe was kept in close contact with the specimen surface. The applied force on the specimen was 0.05 N.

[00207] TGA was carried out on a Dupont Instruments Thermogravimetric Analyzer (951) following the ASTM D3850-94 standard. The sample was ground to a powder after chilling with liquid nitrogen and approximately 20 mg of the specimen was loaded in the open platinum pan. The samples were heated from 25 °C to 600 °C under dry nitrogen at a constant heating rate of 5 °C/min.

Step E – Mechanical Properties

[00208] The tensile property of the PU elastomers was conducted on an Instron 4202 tensile instrument according to the ASTM D882–97 standard. The cross-head speed was 50 mm/min with a load cell of 50 Kgf. At least five identical dumbbell-shaped specimens,

prepared by cutting the material out of a polymer sheet, were tested and the results averaged.

[00209] The compressive properties of the foams were measured on an Instron universal testing machine (model 4202) according to the ASTM D1621–00 standard. The cross-head speed was 3.54 mm/min with a load cell of 500Kgf. The load was applied until the foam was compressed to approximately 15% of its original thickness and the compressive strengths were calculated based on the “10% deformation” method according to the standard. The strengths of five identical specimens per sample were tested and the results averaged.

Step F- Scanning electron microscopy (SEM)

[00210] The microstructure of the obtained PU foams was examined using a Scanning Electron Microscope (Philips XL30 ESEM LaB₆ manufactured by FEI Company, Oregon, USA). Samples are examined uncoated and without processing, with a Gaseous Secondary electron Detector (GSED), within a gaseous environment and a partial vapor pressure of 1.2 mbar. The sample chamber vacuum was around 9.4×10^{-5} mbar. The circular sample was cut into small strips and then snapped by hand to reveal a fracture surface for subsequent microscopy observation.

Step G – Density Test

[00211] The density of the PU foam was determined by averaging the mass/volume measurement results of five specimens per sample. All the samples were run in duplicate for thermomechanical property measurements and in sextuplicate for the tensile, compressive and density tests. The reported errors are the subsequent standard deviations.

Example 5: Modified Methods of Preparation of Polyols from Canola Oil

Step A - Ozonolysis

[00212] Canola oil(100g) and 500ml of ethyl acetate were poured into a specially designed reactor (schematic shown in **Figure 39** and described above), fed with a Direct Current Permanent Magnet 1 HP Motor from Leeson electric-corporation, USA. Ozone was produced in an ozone generator (Azcozon Model RMV16-16 from Azco Industries Ltd, Canada) with oxygen as the feed gas. The reaction was performed at 10°C, at 5 L/min O₂ flow rate and 100 rpm agitation rate. After 1 hour, the ozone generator was stopped and the reaction vessel was purged with N₂ for 10 minutes to remove the unreacted ozone in the vessel. The product was poured out from the reaction vessel for hydrogenation.

Step B – Hydrogenation

[00213] Two catalysts systems were developed.

System A: Palladium-Carbon (10% of weight of Pd in the catalyst) and Raney Nickel

[00214] Palladium catalyst (2g) was added to the ozonide in ethyl acetate in a hydrogenation vessel (2L, Parr Instrument Co, USA) fitted with a magnetic drive. The reaction vessel was flushed 3 times with nitrogen and hydrogen to 200 psi pressure to remove the air and then was charged with hydrogen gas at 200 psi at room temperature. The temperature was increased to 50°C. The consumption of hydrogen was so fast that during the time period the temperature increasing, the pressure in the reaction vessel began to drop. Once the pressure dropped to 100psi, more hydrogen was charged into the reaction vessel until the pressure reached 200psi. After 2 times of recharging the hydrogen, the pressure was constant at 185psi. The total reaction time was 1.5 hours. The temperature was then reduced to room temperature with cooling water and to a final pressure of 170 psi. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The catalyst was filtrated out from the product.

[00215] The product was transferred to the reaction vessel again and 15g Raney Nickel was added. The reaction vessel was flushed 3 times with nitrogen and hydrogen to 400 psi pressure to remove the air and then was charged with hydrogen gas at 300 psi at room temperature. The temperature was increased to 120°C. Once the pressure dropped to 150psi, more hydrogen was charged into the reaction vessel until the pressure reached 200psi. After 2 times of recharging the hydrogen, the pressure was constant at 225 psi. The

total reaction time was 3 hours. The temperature was then reduced to room temperature with cooling water and to a final pressure of 120 psi. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The catalyst was filtrated out from the product.

System B: Zinc Powder and Raney Nickel

[00216] The product from step A was transfer to the hydrogenation vessel and 30g of zinc was also added. 20psi of hydrogen was charged. The mixture was agitated at 4.8RPM and room temperature for 30mins. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The catalyst was filtrated out from the product.

[00217] The product was transferred to the reaction vessel again and 15g Raney Nickel was added. The reaction vessel was flushed 3 times with nitrogen and hydrogen to 300 psi pressure to remove the air and then was charged with hydrogen gas at 250 psi at room temperature. The temperature was increased to 100°C. Once the pressure dropped to 150psi, more hydrogen was charged into the reaction vessel until the pressure reached 250psi. After 5 times of recharging the hydrogen, the pressure constant at 225 psi. The total reaction time was 2.5 hours. The temperature was then reduced to room temperature with cooling water and to a final pressure of 130psi. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The catalyst was filtrated out from the product.

[00218] From GC analysis, the product was not fully hydrogenated. Then the product was transferred to the reaction vessel again and 10g Raney Nickel was added. The reaction vessel was flushed 3 times with nitrogen and hydrogen to 300 psi pressure to remove the air and then was charged with hydrogen gas at 250 psi at room temperature. The temperature was increased to 100°C. Once the pressure dropped to 150psi, more hydrogen was charged into the reaction vessel until the pressure reached 250psi. After recharging the hydrogen once, the pressure was constant at 190 psi. The total reaction time was 2.5 hours. The temperature was then reduced to room temperature with cooling water and to a final pressure of 135psi. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The catalyst was filtrated out from the product.

[00219] The wiped-blade molecular distillation and GC, HPLC analysis methods are the same as in Example 2: Step C, Step D and Step F, except that A HPLC run consisted of a linear gradient of 100% solvent A to 70% A and 30% solvent B in 30 min.; then back to 100% A in 1 minutes at a flow rate of 2 mL/min.

[00220] It was also found that the ethyl acetate recycled by rotary evaporator can be successfully applied as a solvent for ozonolysis and hydrogenation reactions.

[00221] For both system A and system B, a batch of vegetable oils treated as described in the current example, i.e. full ozonolysis with an ozone flow of 5 L/min and subsequent full hydrogenation, results in a polyol product constituted by 95% triol and 5% of mono-ol and diol

Step C – Rheometric Measurements

[00222] The viscosities of the polyol samples were measured in shearing mode with the Universal Dynamic Rheometer PHYSICA UDS 200 (Paar Physica USA) with a constant shearing rate of 51.6 s^{-1} . The viscosities were recorded at 6 different temperatures, from 50 °C to 25 °C every 5 °C. The viscosities were also measured at 25 °C as a function of time.

Step D - Hydroxyl and acidity values

[00223] The hydroxyl numbers of the polyols were determined according to the ASTM titration method D1957-86 and the acidity values were determined according to the ASTM method D4662-98. Triplicate specimens were measured for each polyol and the average values and standard deviations are reported here.

[00224] In this example, properties of PU rigid foams prepared by reacting polyols synthesized from canola oils by using ethyl acetate and recycled ethyl acetate with aromatic diisocyanates are described. The relevant parameters of the polyols and diisocyanates are listed in **Table 10**.

Table 10. The parameters of the used polyols and diisocyanate.

	Equivalent weight (g/mole)	OH number (mg KOH/g)	Acidity number (mg KOH/g)
Canola based polyol (ethyl acetate)	229	245.5 ± 2.2	10.6 ± 0.1
Canola based polyol(recycled ethyl acetate)	299	187.8 ± 2.6	25.6 ± 0.1
MDI	133		

Step E - Preparation of the Polyurethanes

[00225] The polyols synthesized with the modified ozonolysis and hydrogenation methods set out in **Example 5** were used to produce PU foam samples. They are referred to as Ethyl Acetate Canola Oil Based PU (EACOBPU) for the polyols synthesized using ethyl acetate as solvent and Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU), for the polyols synthesized using recycled ethyl acetate respectively.

[00226] The formulation used to prepare foams is the same as shown in **Table 9**. The polyols were reacted with MDI, in the presence of Dibutyl Dilaurate (DBTDL) from Aldrich Chemical (USA) as the main catalyst, N, N- Dimethylethanolamine (DMEA) from Aldrich Chemical (USA) as the co-catalyst, and glycerin from Fisher Chemicals (USA) as cross-linker agents and distilled water as blowing agent. The surfactant was B-8404 from Goldschmidt Chemical Canada. The specific polyol was first mixed (2 minutes) in a plastic container with suitable amounts of crosslinkers, catalyst, and surfactant. MDI was added and the mixture was stirred vigorously for 60 seconds in the case of EACOBPU foams and for 50 seconds in the case of REACOBPU foams. The mixture was then poured into a home-made TEFLON mould which was greased with the silicon release agent and sealed with a hand-tightened clamp. After the reaction had been completed, the sample was post cured at room temperature for 4 days.

[00227] For the compressive property measurements, foams samples were prepared in circular cylindrical TEFLON molds of 60-mm diameter and 36-mm long. For DMA measurements, rectangular samples were prepared with the same procedure by polymerizing the reactants in (18×13×4 mm)-TEFLON molds.

[00228] DMA measurements were carried out on a TA Instrument DMA Q800 equipped with a liquid nitrogen cooling apparatus, in the single cantilever mode, with a constant heating rate of 1°C/minute from -120°C to +50°C. The measurements were performed following ASTM E1640-99 standard at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.015 mm.

[00229] The compressive properties of the foams were measured on an Instron universal testing machine (model 4202) according to the ASTM D1621-00 standard. The cross-head speed was 3.54 mm/min with a load cell of 500Kgf. The load was applied until the foam was compressed to approximately 15% of its original thickness and the compressive strengths were calculated based on the “10% deformation” method according to the standard. The strengths of five identical specimens per sample were tested and the results averaged.

[00230] The density of the PU foam was determined by averaging the mass/volume measurement results of five specimens per sample. All the samples were run in duplicate for thermomechanical property measurements and in sextuplicate for the tensile, compressive and density tests. The reported errors are the subsequent standard deviations

Example 6: General Procedure for Preparation of Estolides

Step A: Ozonolysis

[00231] Canola oil (100g) and 400ml of distilled water were poured into the reactor (schematic shown in **Figure 39**), fed with a Direct Current Permanent Magnet 1 HP Motor from Leeson electric-corporation, USA. Ozone was produced in an ozone generator (Azcozon Model RMV16-16 from Azco Industries Ltd, Canada) with oxygen as the feed gas. The reaction was performed at 27°C, at 5 L/min O₂ flow rate and 80 rpm agitation rate.

After 5 hours, the ozone generator was stopped and the reaction vessel was purged with N₂ for 10 minutes to remove the unreacted ozone in the vessel. The product was poured out and transferred into a separatory funnel to remove the aqueous layer.

Step B: Hydrogenation

[00232] The short chain alcohols collected from the previous batches through the molecular blade distillation was used as the hydrogenation solvent. About 400g of this solvent was added to the ozonide in the ozonolysis vessel and agitated under the nitrogen for 1 hour to ensure the ozonide was completely dissolved in the solvent. Then this solution was transferred to the hydrogenation vessel (2L, Parr Instrument Co, USA). 14.3 g of Raney nickel catalyst were added to the ozonide solution. The reaction vessel was flushed 3 times with nitrogen at 200 psi pressure to remove the air and then was charged with hydrogen gas at 350 psi at room temperature. The temperature was increased over 30 minutes to 135°C with a concomitant increase in pressure to 490 psi. The hydrogenation reaction was carried for 5.5 hours at this temperature and the pressure decreased with the consumption of hydrogen. The temperature was then reduced to room temperature with cooling water and the pressure reduced to a final pressure of 235 psi. The unreacted hydrogen gas was removed from the reaction vessel with nitrogen gas. The remaining mixture was filtered over Celite and the aqueous layer removed in a separatory funnel.

Step C: Wiped-blade Molecular Distillation

[00233] The wiped blade molecular distillation unit (Model VKL 70/ICL-04, from Incon Processing) was set up at a jacket temperature of 115°C, and the temperature of the condenser 30°C. The pressure of the distillation system was reduced to 20 mTorr and the viscous oily product added into the distillation system through an addition funnel at a speed of 1mL/min. After all the product had been added to the distillation system, the unit was kept running for 30 minutes, to allow the complete collection of the residue and distillate. Finally, distillate (140.0g) and residue (52.0g) were obtained.

Step D: Flash Chromatography

[00234] A column of dimensions 3 id × 30cm was packed with 400g (about 212 mL volume) of silica gel (230-400 mesh). Material from the residue fraction of distillation

(1.7g) was added. The column was then eluted under air pressure with gradient flow phase composed of hexane and ethyl acetate. The ratios (v/v) of hexane to ethyl acetate was started with 50:1, then gradually decreased to 25:1, 20:1, 12:1, 10:1, 8:1, 7:1, 5:1, 3:1, followed by 2:1, 1:1, 1:2. Finally pure ethyl acetate was used and the fractions were collected in 20mL-test tubes. Thin layer chromatography (TLC) was run on each fraction using hexane and ethyl acetate as the developing system with ratios (v/v) of hexane and ethyl acetate of 3:1, 2:1, and 1:1. The glycerides and related compounds were detected by spraying the plates first with methanol containing 10% sulphuric acid (concentration 98%) and then heating them at 200°C for 5 minutes. A ratio of flow phase of 7:1 was used on fractions 110-130. The estolide is in this fraction.

CLAIMS

1. A method for the production of a polyol from a renewable feedstock comprising one or more unsaturated fatty acid triacylglycerols, wherein the method comprises the steps of:
 - a. ozonolysis of two or more double bonds in the unsaturated fatty acids found in the triacylglycerols of the feedstock under conditions effective to afford two or more corresponding ozonides; and
 - b. reductive hydrogenation under conditions effective to afford hydrogenation of the products of step (a) to afford one or more corresponding polyols, wherein the one or more polyols comprise a triacylglycerol containing at least two primary hydroxyl groups.
2. The method of claim 1, wherein the one or more polyols comprise a dihydroxyl functionalized triacylglycerol, or a trihydroxyl functionalized triacylglycerol, or mixtures thereof.
3. The method of claim 1, wherein the feedstock comprises a vegetable oil or tallow.
4. The method of claim 3, wherein the vegetable oil is selected from the group comprising canola, linseed, sunflower, tung, lesqueralla, flaxseed, Jatupha, camelina sativa, hump, peanut, palm, soy, cottonseed, corn, cashew nuts, calendula, mustard, sesame, safflower, sunflower, rapeseed, olive, castor, jojoba, brazil nuts, avocado, and kenaf.
5. The method of claim 1, wherein the feedstock comprises soy.

6. The method of any one of claims 1 -5, further comprising the step of separating the one or more polyols from the reaction mixture of step (b) to afford substantially pure and isolated polyols.
7. The method of claim 6, wherein the one or more polyols produced are isolated in greater than 90% purity relative to non-polyol components contained in or produced during the production of the one or more polyols.
8. The method of claim 7, wherein the one or more polyols produced are isolated in greater than 95% purity relative to non-polyol components contained in or produced during the production of the one or more polyols.
9. The method of claim 6, wherein the separation step comprises the use of silica gel chromatography.
10. The method of claim 6, wherein said method further comprises the production of one or more short chain alcohols as a by-product of said reaction and said one or more short chain alcohols is separated from the one or more polyols.
11. The method of claim 10, wherein said separation of said short chain alcohol product is carried out prior to separation of said one or more polyols.
12. The method of claim 11, wherein said separation step for separating said short chain alcohols comprises the use of wiped-blade molecular distillation.

13. The method of any one of claims 1-12 wherein ethyl acetate is used as the solvent during the ozonolysis step.
14. A method for producing a polyurethane polymer which comprises reacting a polyol prepared by the methods of any one of claims 1 - 13 with a suitable isocyanate to afford said polyurethane polymer, with the proviso that where said polyol is a flax-based polyol, said polyurethane polymer is not a foam.
15. The method of claim 14, wherein the polyurethane polymer comprises an elastomer, a resin, a plastic, a flexible slab, or a foam.
16. The method of claim 15, wherein said foam is rigid or flexible.
17. The method of claim 16, wherein said foam is a flexible moulded foam.
18. The method of claim 15, wherein said resin is a rigid set resin.
19. The method of claim 15, wherein said plastic comprises an elastomer.
20. A polyurethane polymer prepared by the method of claim 14, with the proviso that where said polyol is a flax-based polyol, said polyurethane polymer is not a foam.

21. A method for the production of nonanol, hexanol, propanol, and 1,3-propanediol from a renewable feedstock comprising a fatty acid triacylglycerol having at least one unsaturated fatty acid chain, the method comprising the steps of:
- a. ozonolysis of the double bonds in the fatty acid chain of the triacylglycerol of the feedstock;
 - b. reductive hydrogenation of the ozonide product formed in step (a) to produce nonanol, hexanol, propanol, and 1,3-propanediol; and
 - c. separating nonanol, hexanol, propanol, and 1,3-propanediol from the hydrogenated product formed in step (b) by wiped-blade molecular distillation.
22. The method of claim 21, wherein the feedstock comprises canola oil.
23. A method for the production of an estolide from a renewable feedstock comprising one or more unsaturated fatty acid triacylglycerols, wherein the method comprises the steps of:
- a. ozonolysis of the double bonds in the unsaturated fatty acids found in the triacylglycerols of the feedstock;
 - b. reductive hydrogenation of the products of step (a) to produce the corresponding polyol in the presence of a short chain alcohol;
- wherein the polyol comprises a triacylglycerol containing at least one terminal hydroxyl group, and wherein the reaction conditions are sufficient to afford transesterification between the polyol and the short chain alcohol, thereby affording said estolide.

24. The method of claim 23, wherein said short chain alcohol contains 9 carbons.
25. The method of claim 23, wherein said short chain alcohol is produced as a by-product in the preparation of said polyol from said feedstock.
26. The method of claim 23, wherein said short chain alcohol is used as a solvent in the hydrogenation reaction.
27. An improved apparatus for carrying out ozonolysis reactions, said improvement comprising:
- a longitudinally disposed agitator operatively connected to a motor, said longitudinally disposed agitator comprising a plurality of pitched blades,
 - wherein said longitudinally disposed agitator extends downwardly into a reaction vessel having an upper and a lower end,
 - said reaction vessel comprising an ozone inlet channel disposed at the lower end and extending across the diameter of said reaction vessel,
 - said ozone inlet channel having two apertures for ozone input at opposing ends thereof and a plurality of pores for release of ozone into said reaction vessel.
28. The apparatus as claimed in claim 27, wherein said longitudinally disposed agitator comprises 6 pitched blades.
29. The apparatus as claimed in claim 27 or 28, wherein the pitched blades extend from said longitudinally disposed agitator at an angle of from about 30 degrees to about 60 degrees relative to the longitudinal axis of the longitudinally disposed agitator.

30. The apparatus as claimed in claim 29, wherein the pitched blades extend from said longitudinally disposed agitator at an angle of about 60 degrees.

31. The apparatus as claimed in any of claims 27 to 30, wherein the pitched blades are trapezoidal in shape.

32. The apparatus as claimed in any of claims 27 to 31, wherein the pitched blades contain a plurality of holes therein.

33. The apparatus as claimed in claim 32, wherein the pitched blades contain 6 holes.

34. The method of claim 1, wherein the ozonolysis conditions are selected in order to produce polyols for forming polyurethane products having harder or softer properties.

35. The method of claim 34, wherein said ozonolysis conditions comprise at least one of ozonolysis time, ozone flow rate, and concentration of the renewable feedstock.

Application number/numéro de demande: 2531977

Figures: 6-32ABC

Pages: _____

DRW-TP

Unscannable items
received with this application
(Request original documents in File Prep. Section on the 10th Floor)

Documents reçus avec cette demande ne pouvant être balayés
(Commander les documents originaux dans la section de préparation des dossiers au
10ième étage)

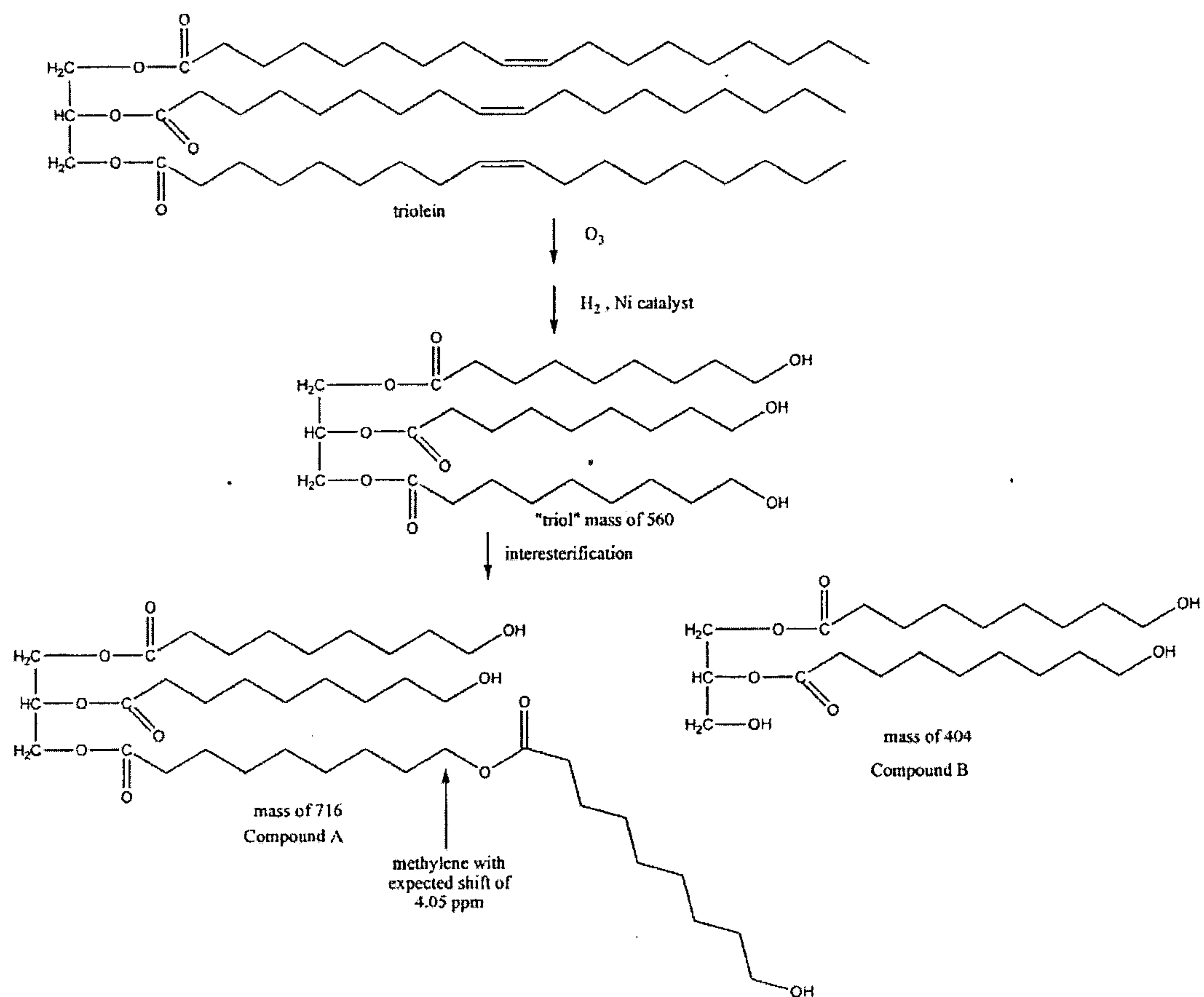
Figure 1: Production of Polyol and Subsequent Interesterification

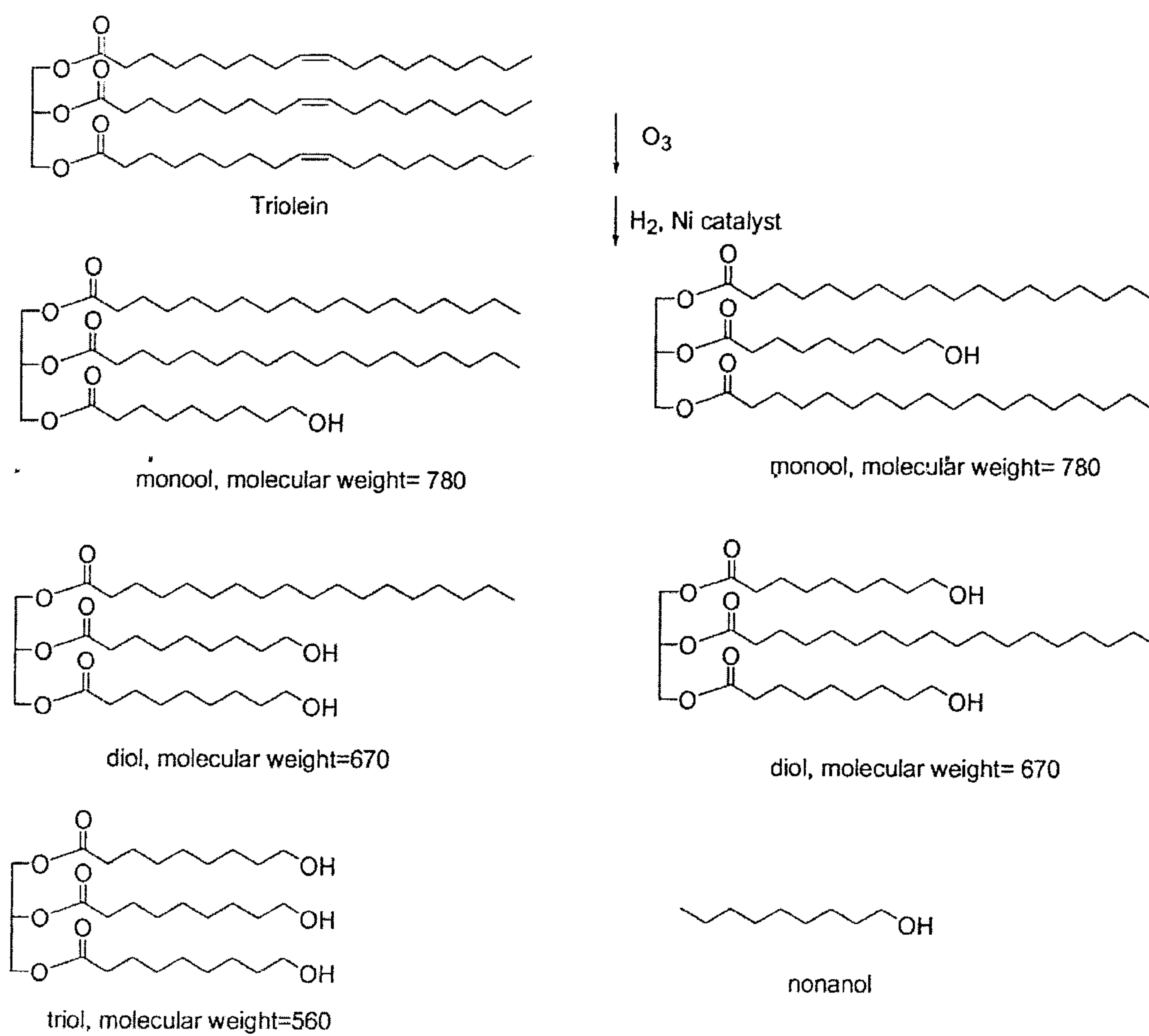
Figure 2: Synthesis reaction of Polyols from Canola Oil

Figure 3: HPLC of Reaction Mixture (upper trace) and Fraction 76 (lower trace) After Hydrogenation

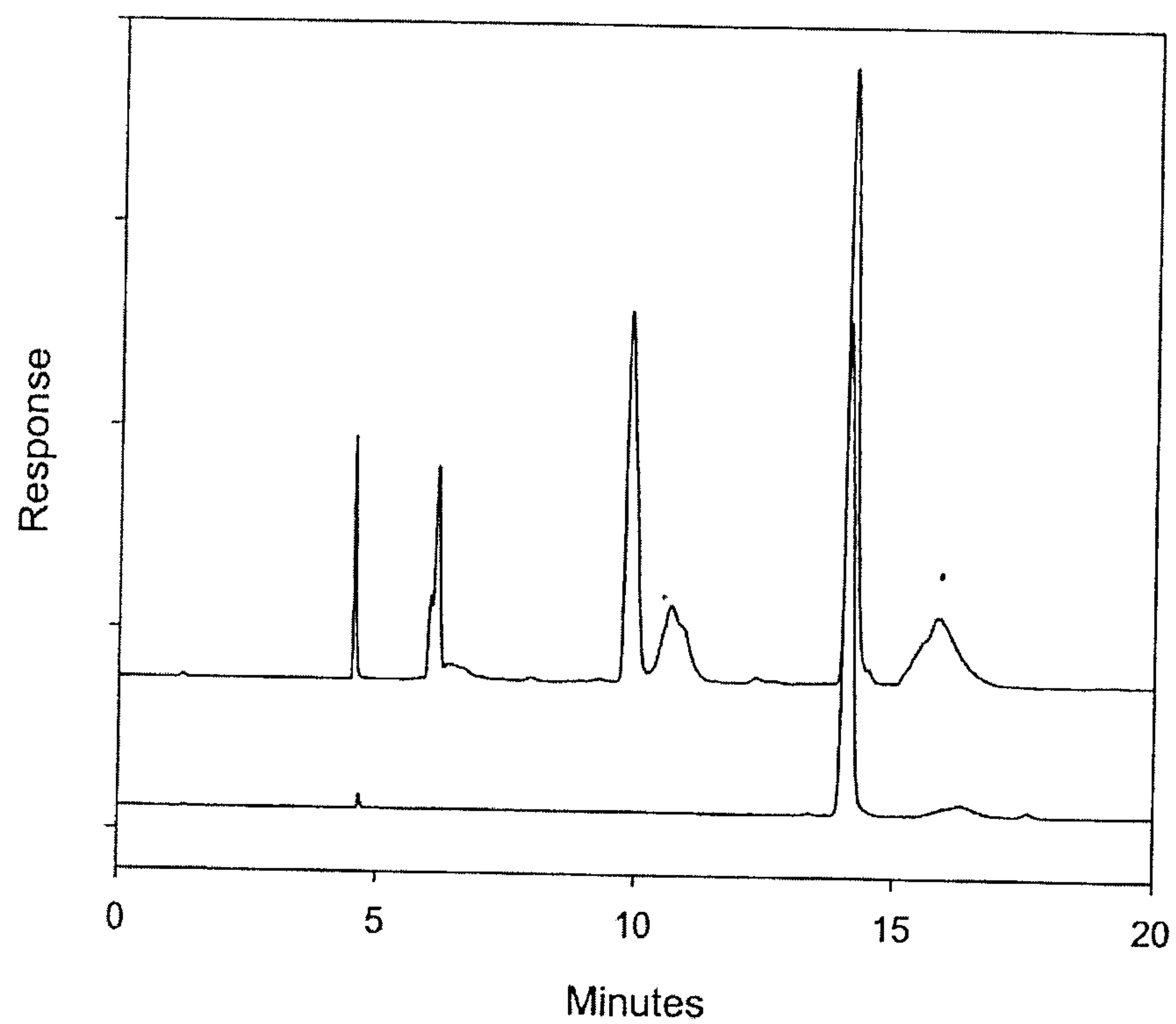
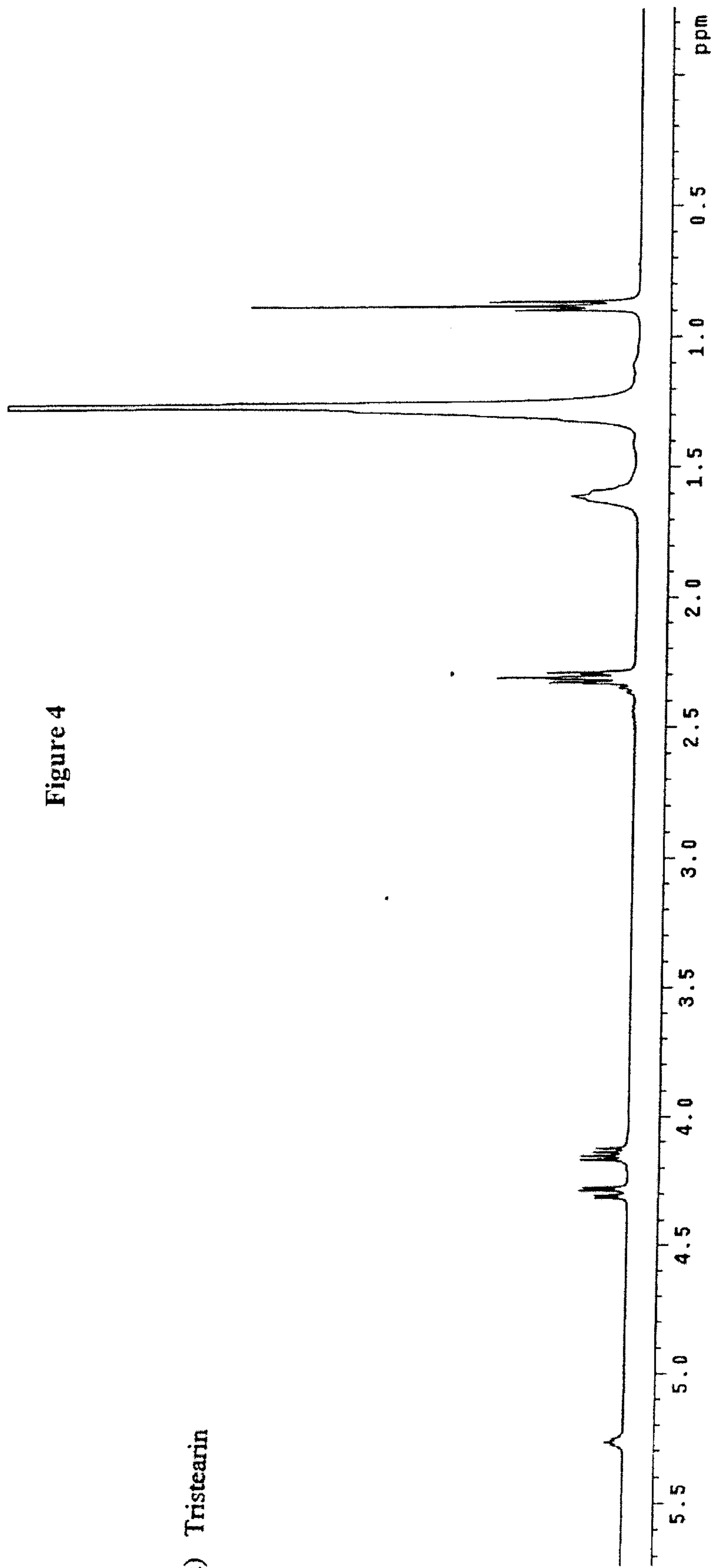


Figure 4

a) Tristearin



b) Frac 76

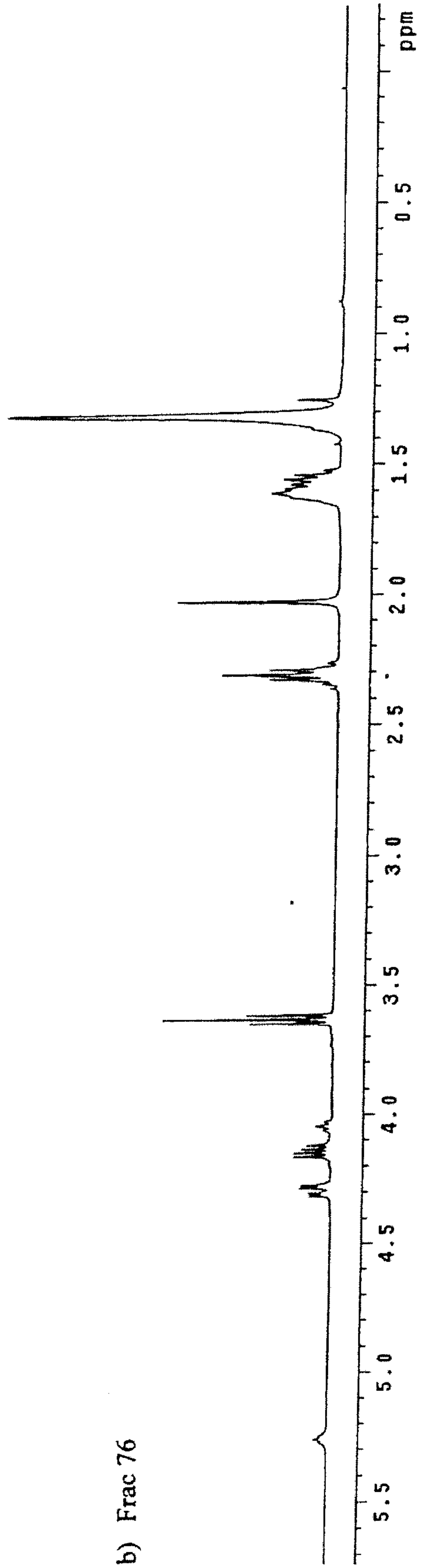


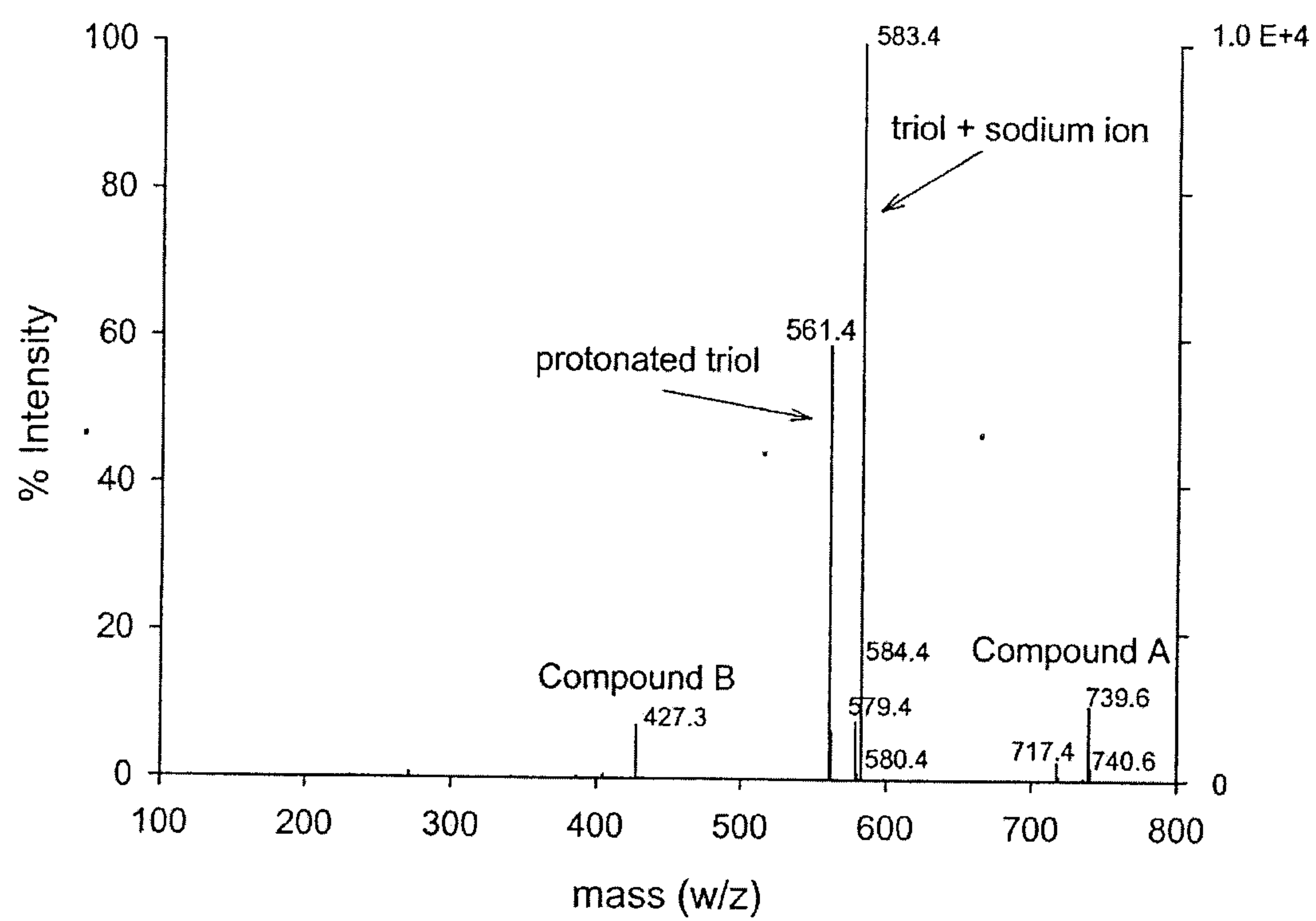
Figure 5: Electrospray Ionization Mass Spectrometry of Fraction 76

Figure 7: GC of Products of First and Second Hydrogenation

(A) Product after First Hydrogenation

(B) Product after Second Hydrogenation

1= Nonanal, retention time= 5.7min

2= Nonanol, retention time= 8.4 min

3= Nonanoic acid, retention time= 13.7min

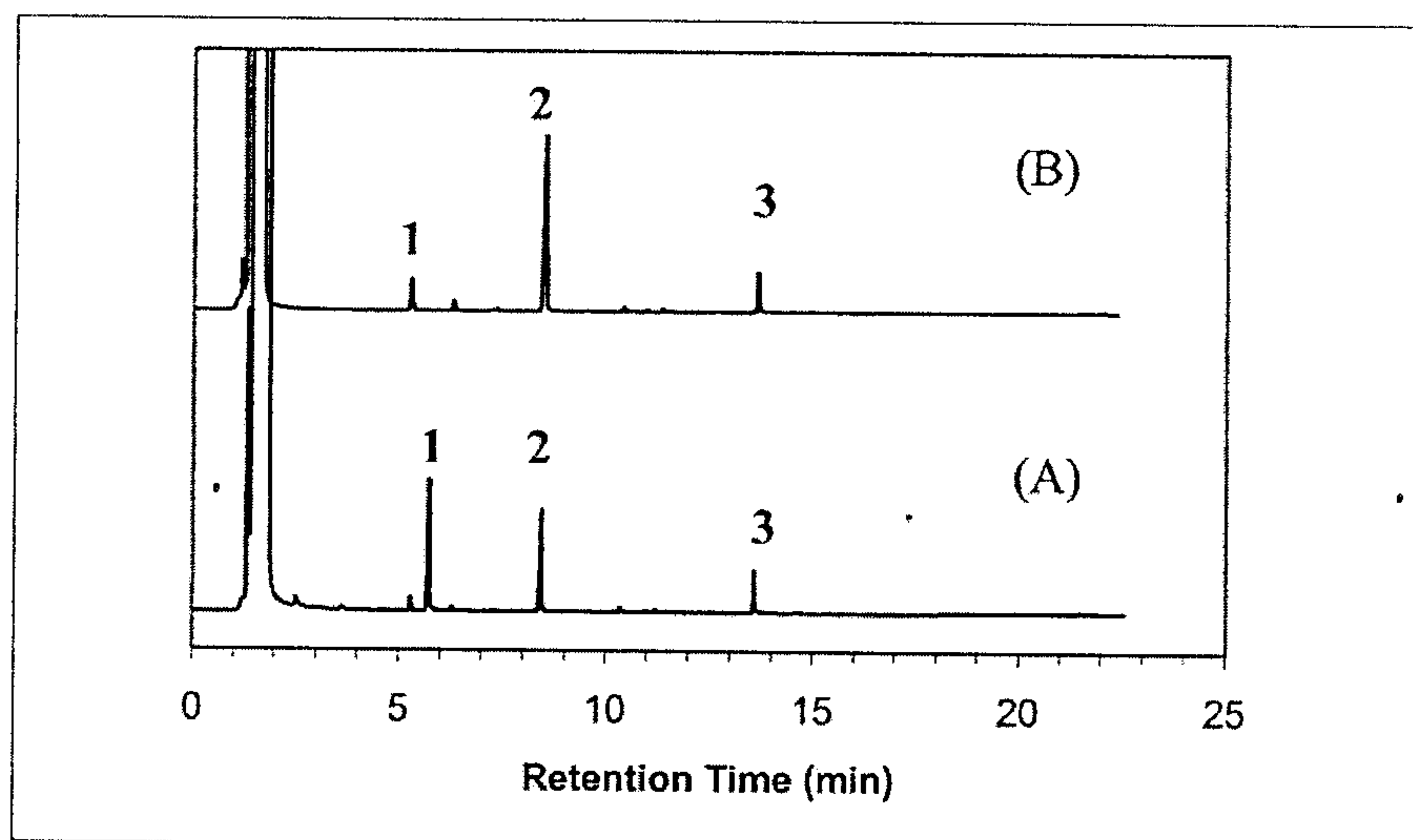


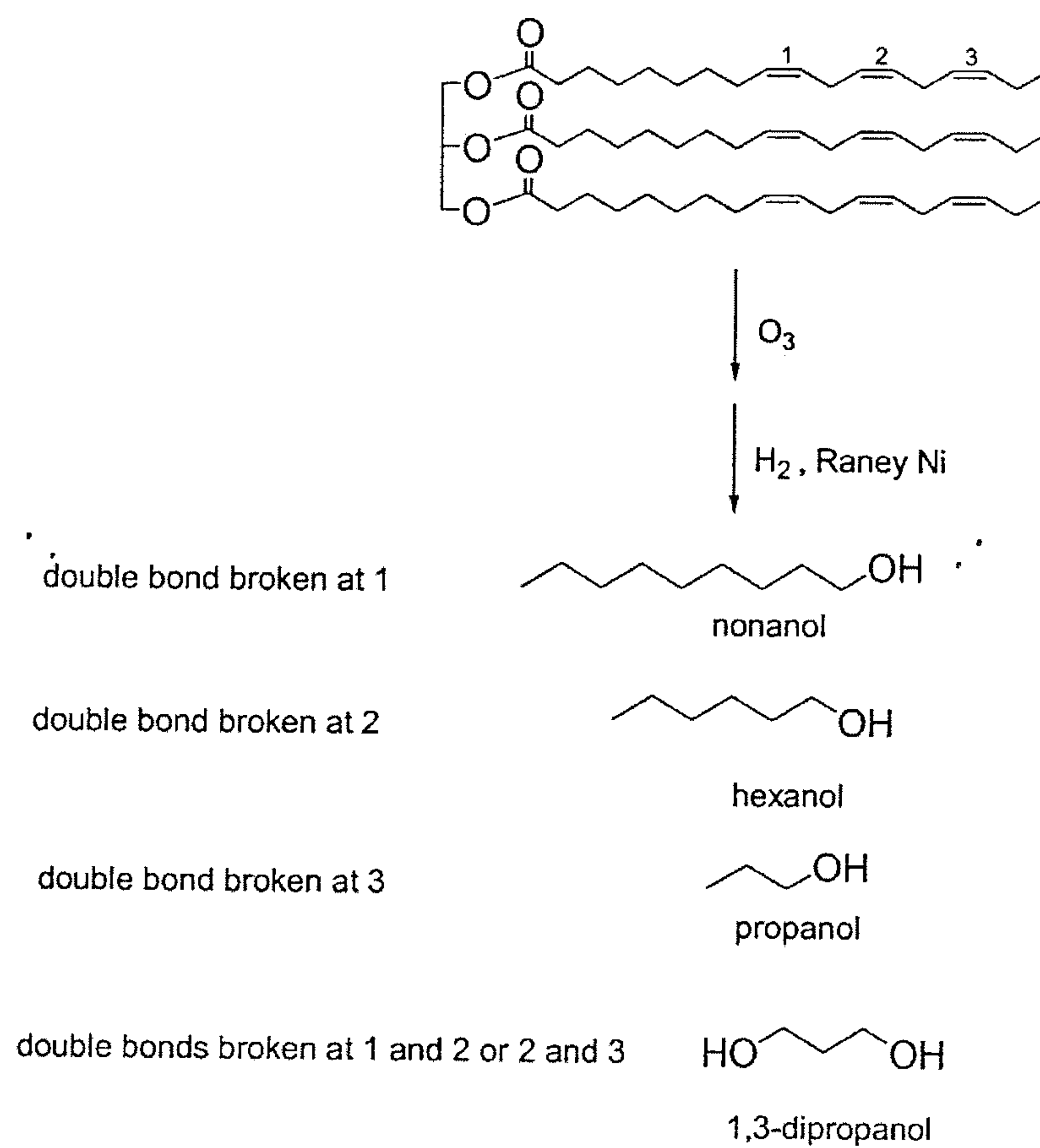
Figure 8: Side Products from Canola Oil

Figure 9: GC of Products before and after Distillation

(a) before Distillation

(b) after Distillation

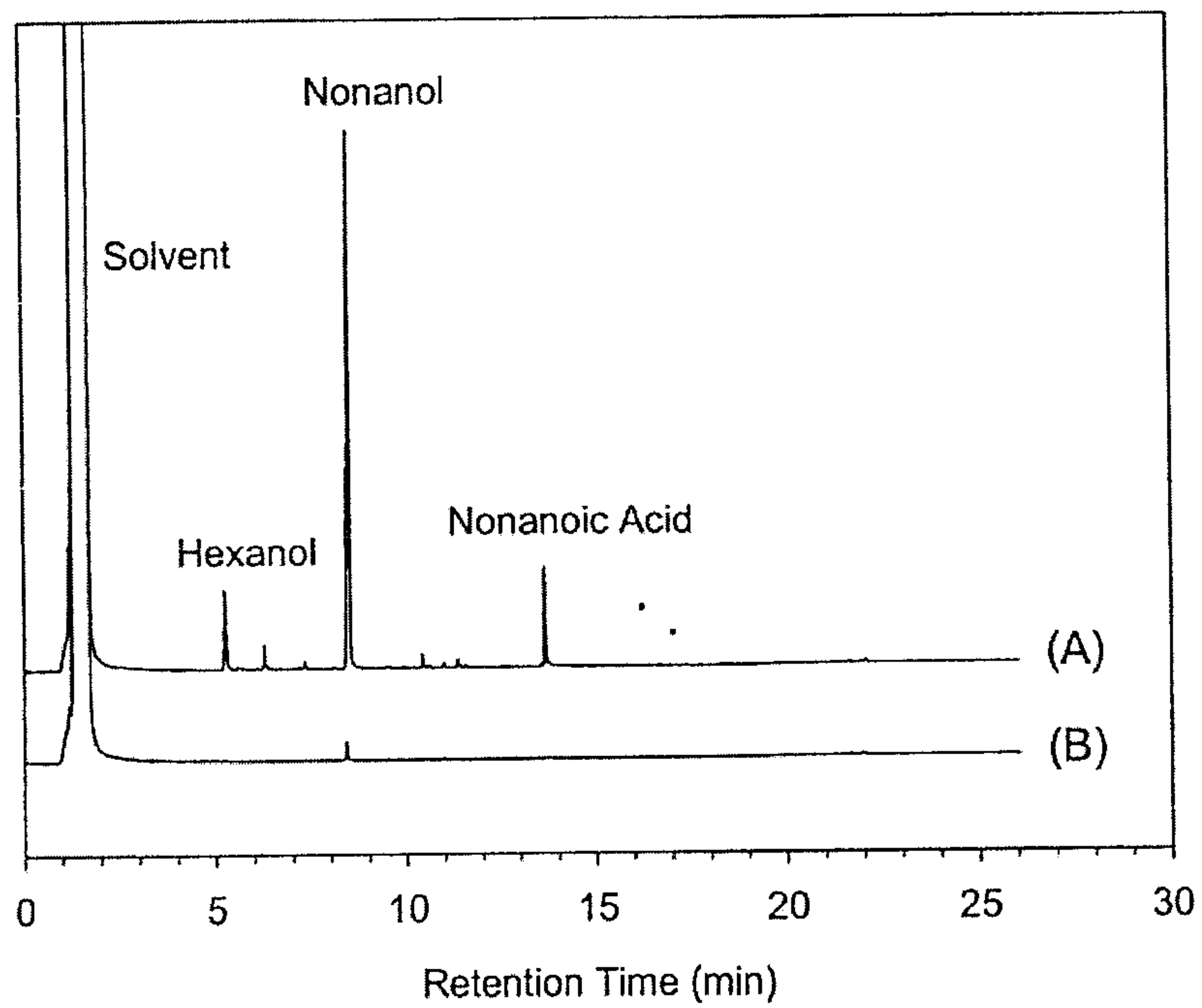


Figure 10: HPLC of Polyol Product.

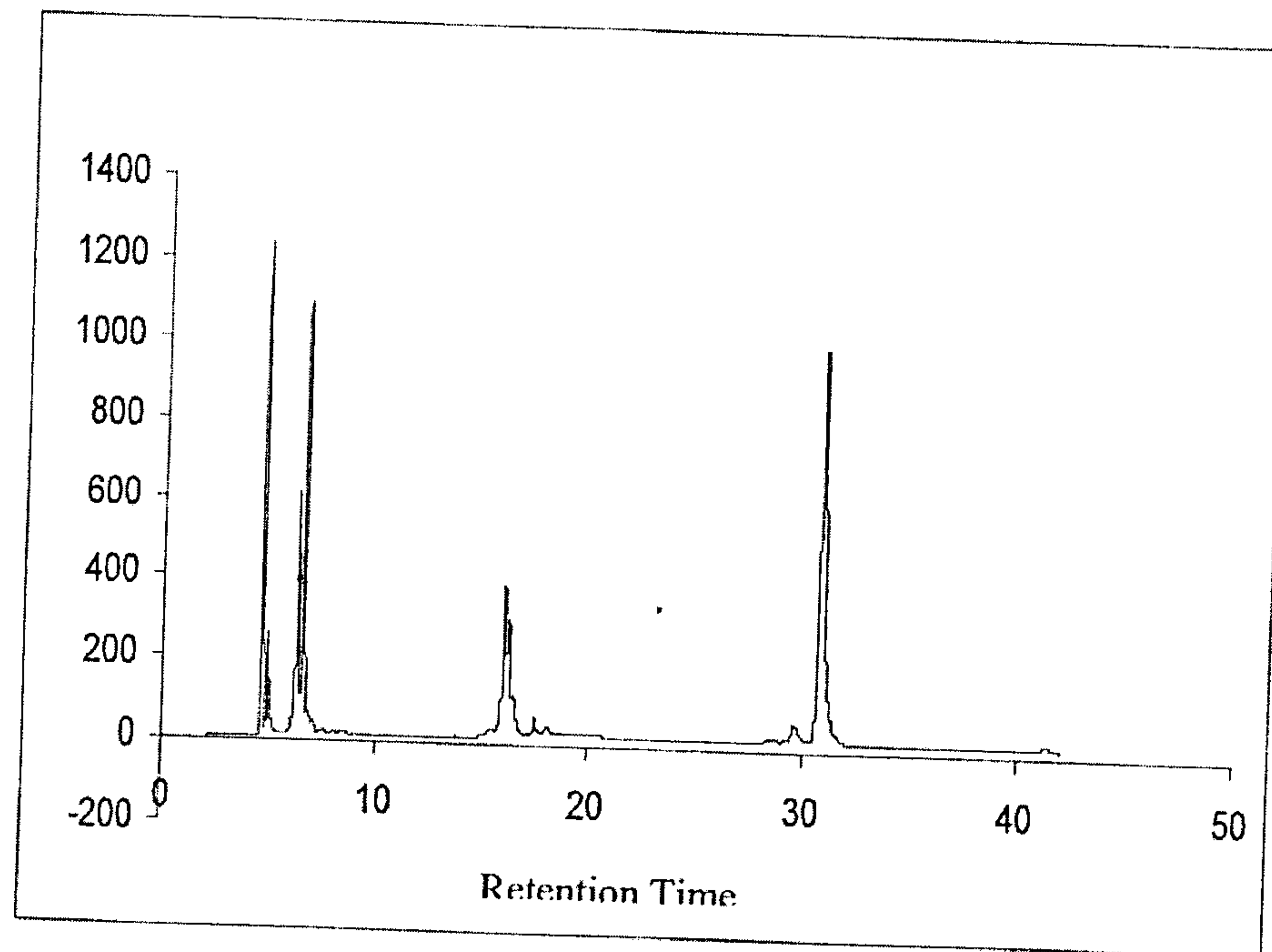


Figure 11: HPLC of Triacylglycerol, Mono-ol, Diol and Triol

Sample A: Triacylglycerol

Sample B: Mono-ol

Sample C: Diol

Sample D: Triol

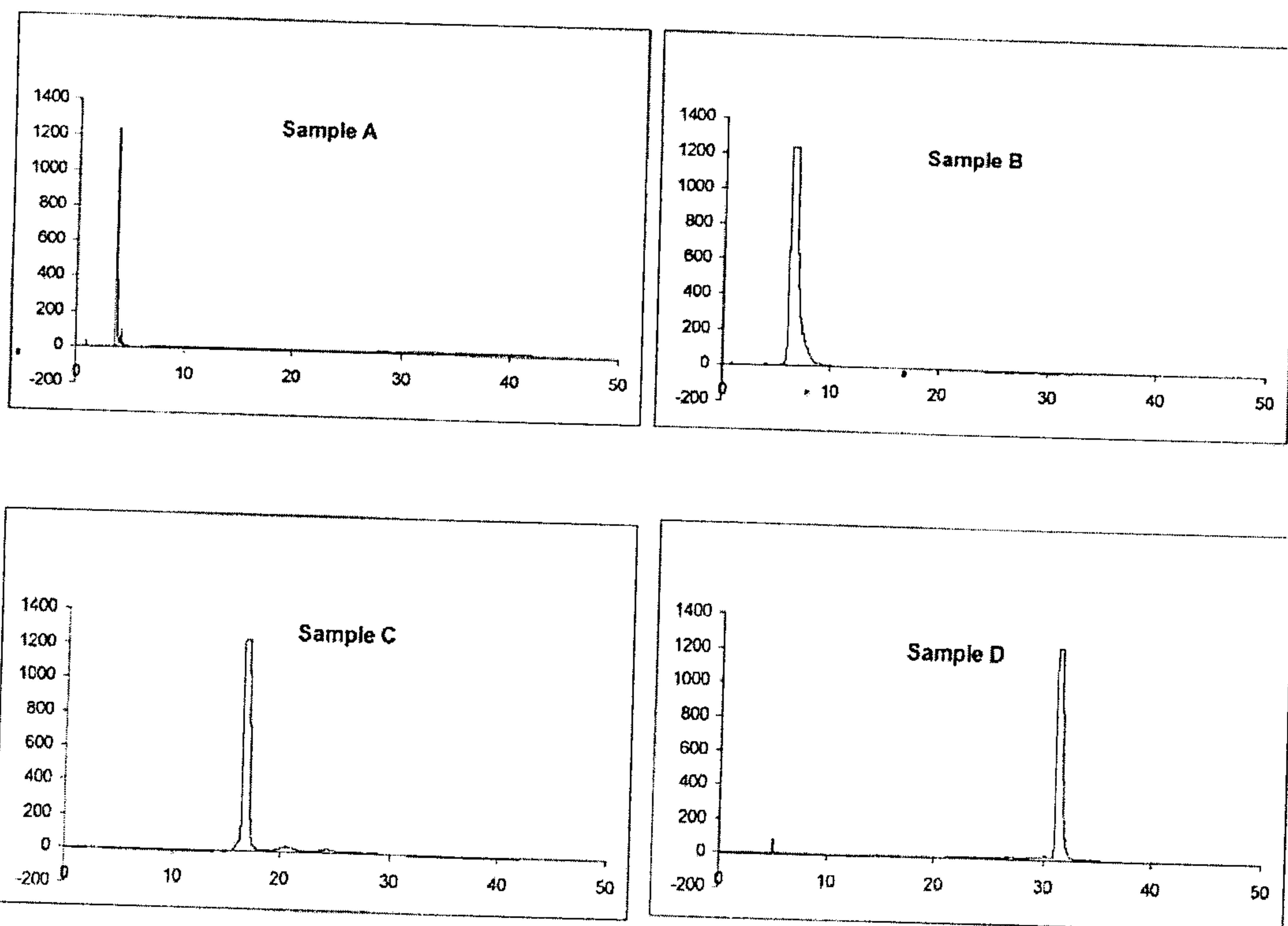


Figure 12: FTIR spectra of Triacylglycerol, Mono-ol, Diol and Triol

A: Triacylglycerol

B: Mono-ol

C: Diol

D: Triol

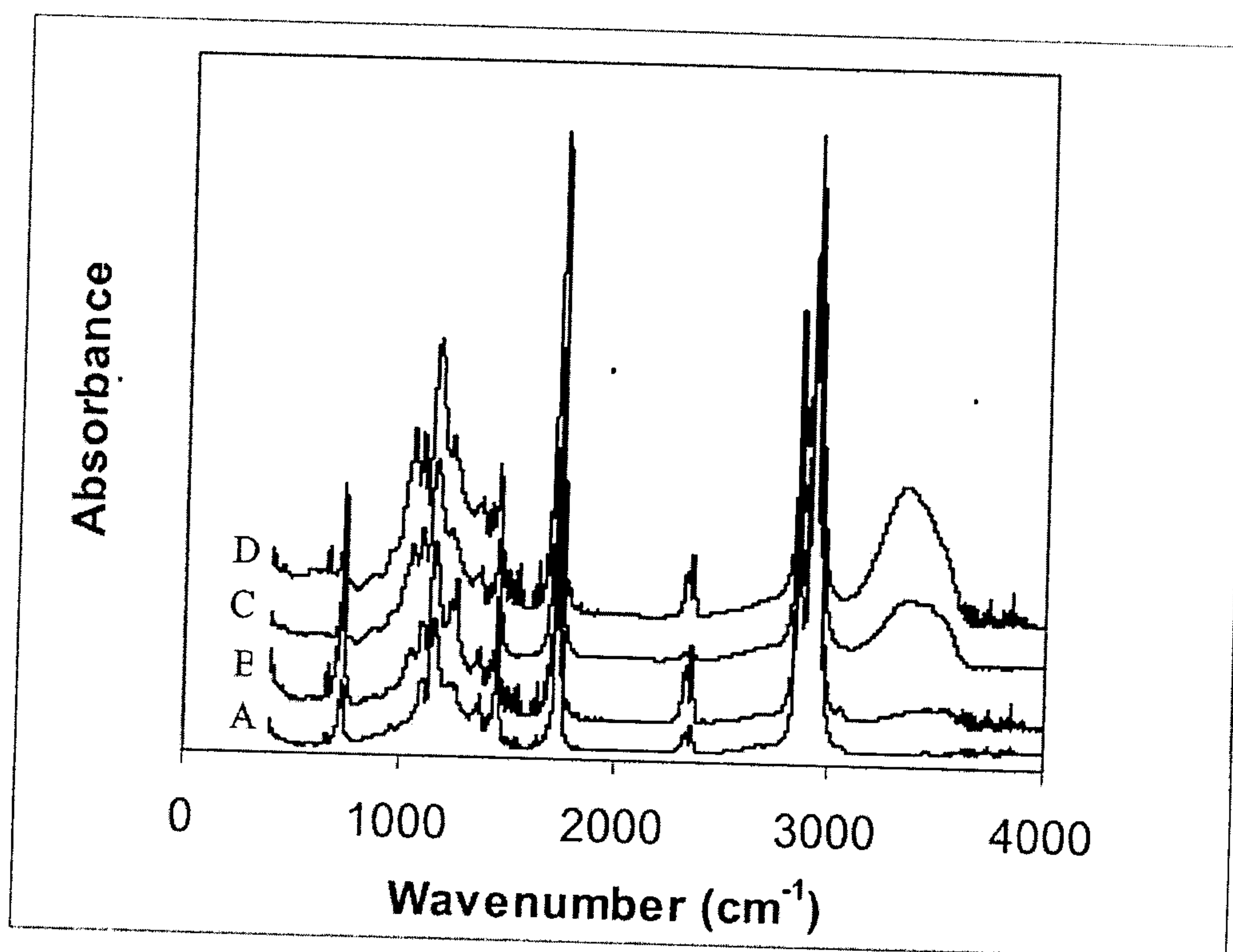


Figure 13: ^1H -NMR of Triacylglycerol, Mono-ol, Diol and Triol

A: Triglycerol

B: Mono-ol

C: Diol

D: Triol

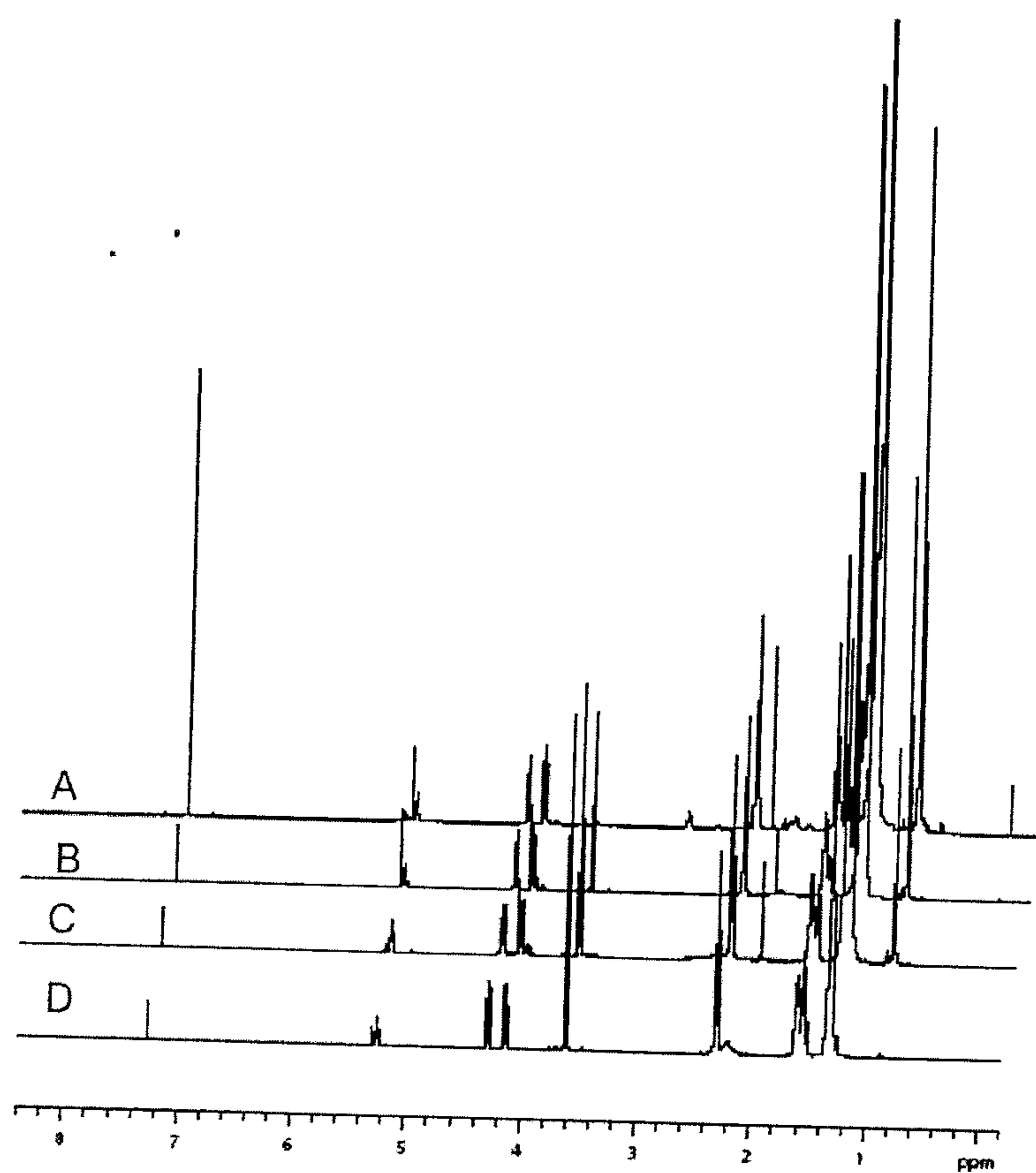


Figure 14: Mass Spectrometry of Mono-ol, Diol and Triol

Sample B: Mono-ol

Sample C: Diol

Sample D: Triol

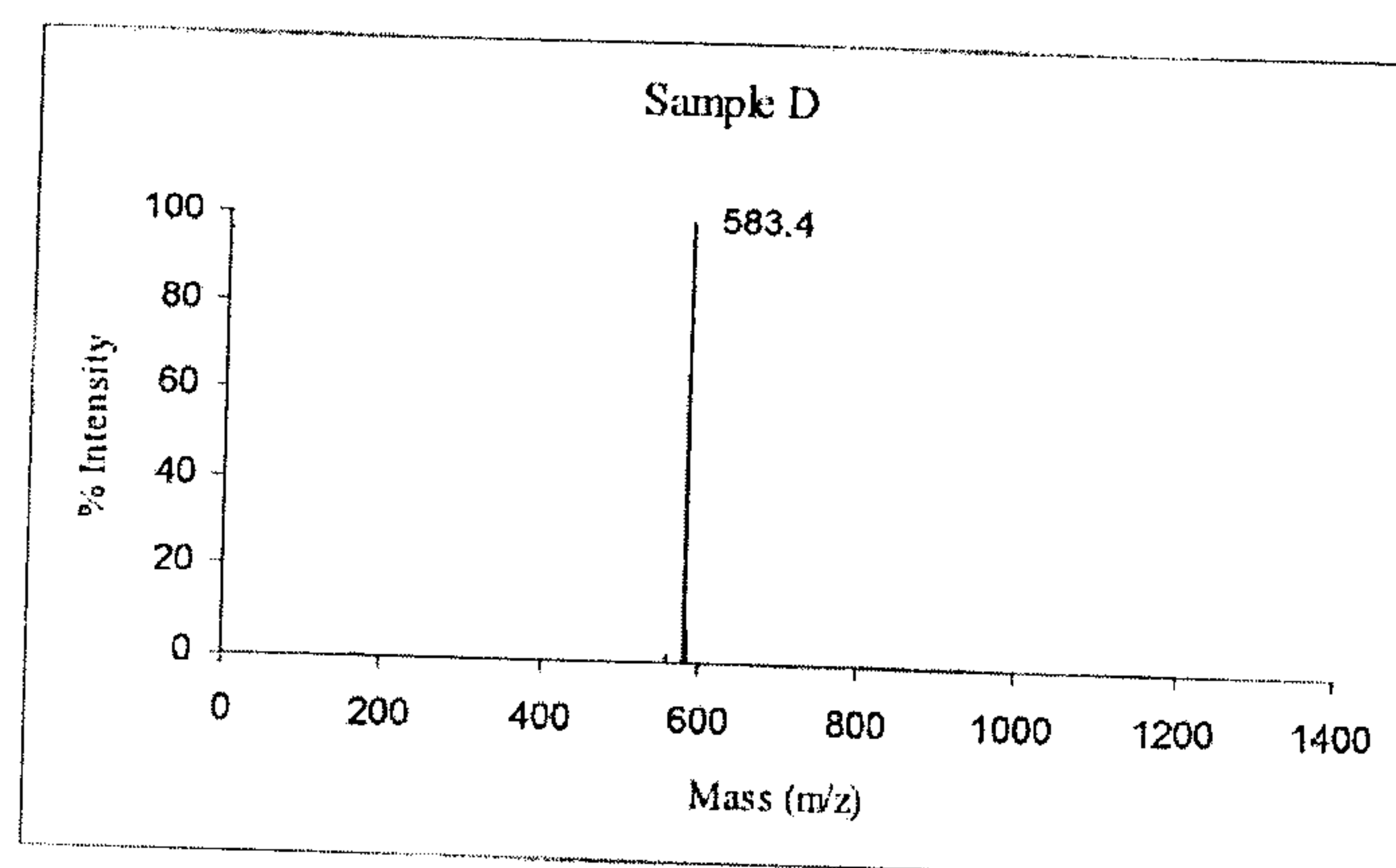
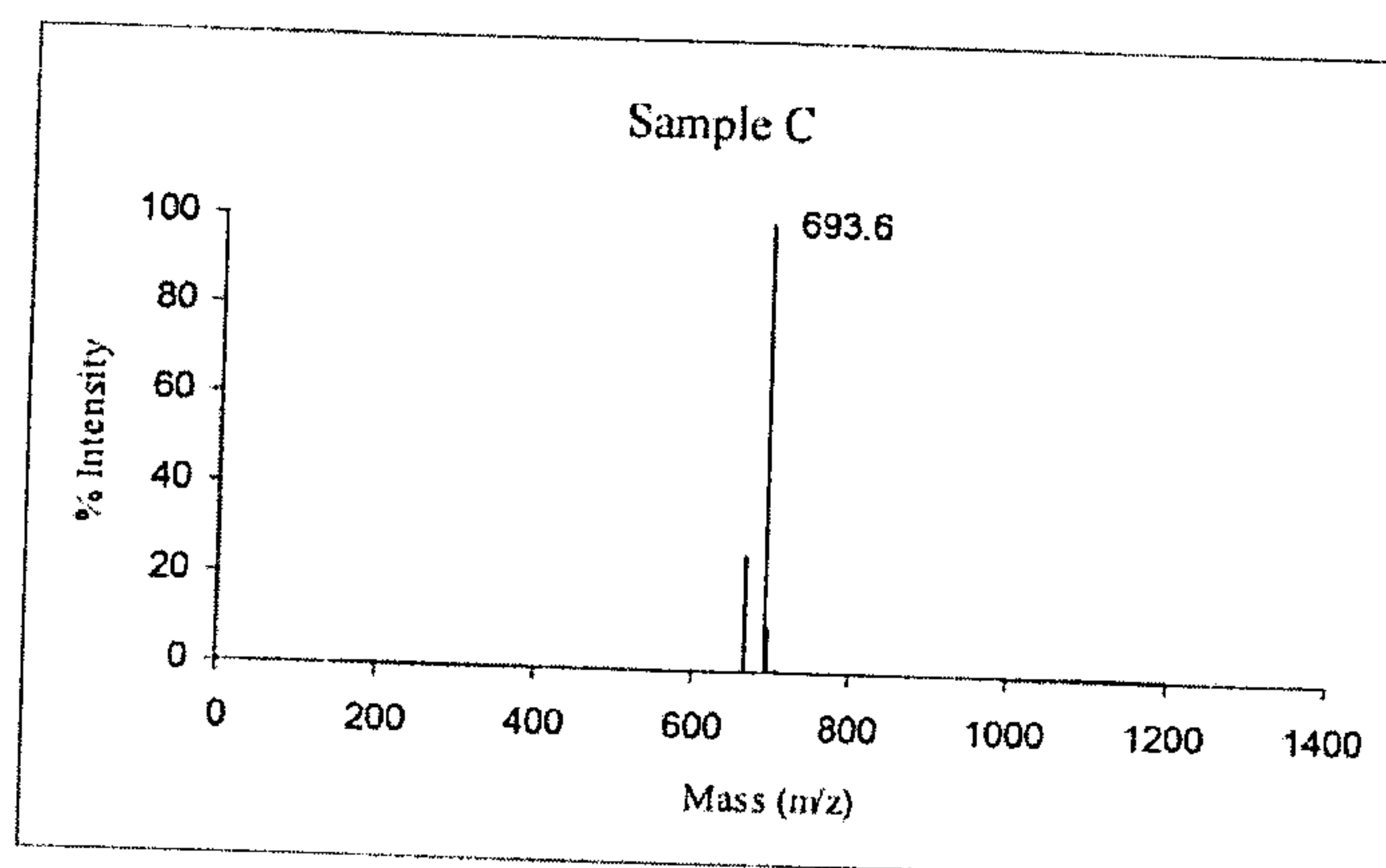
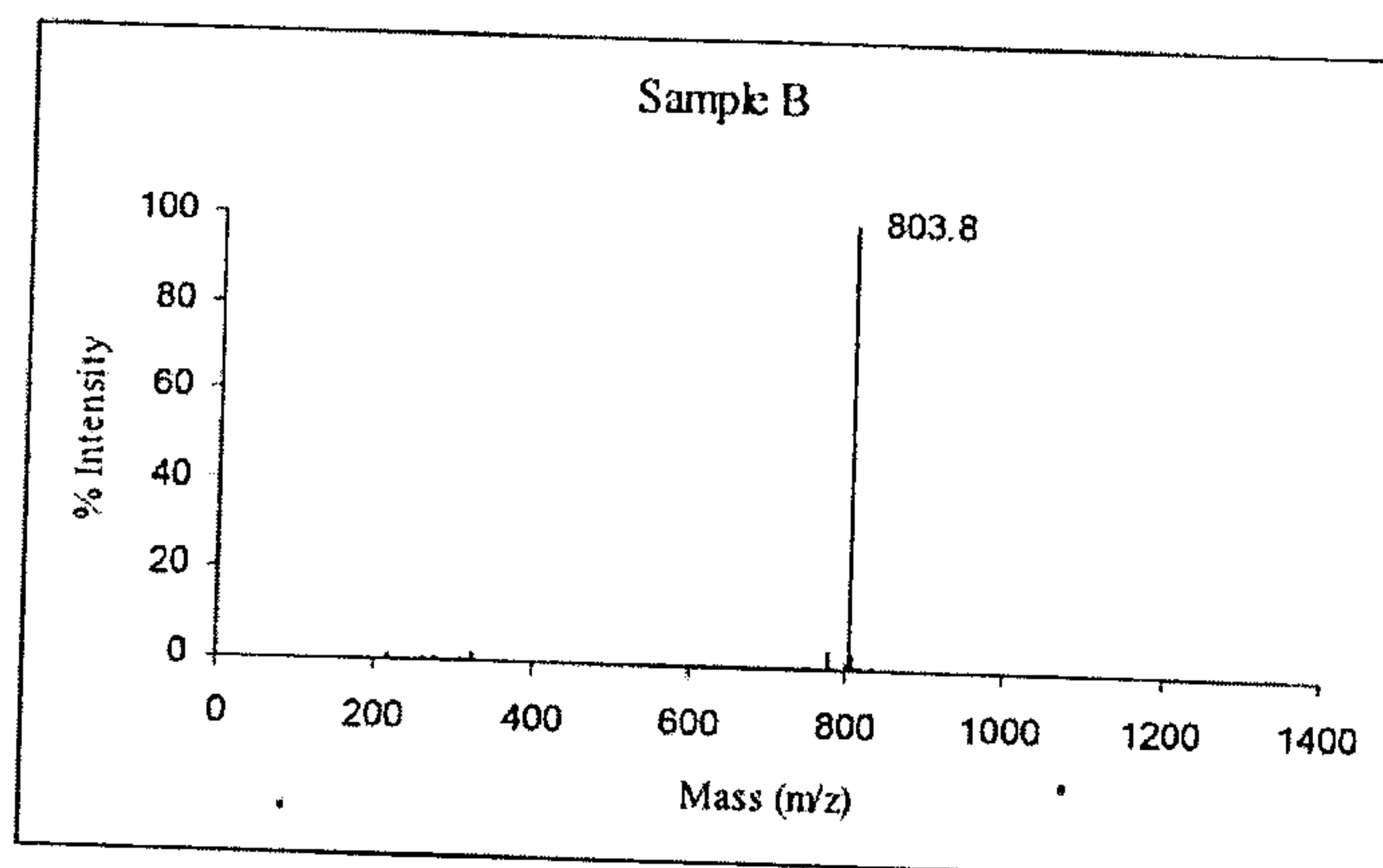


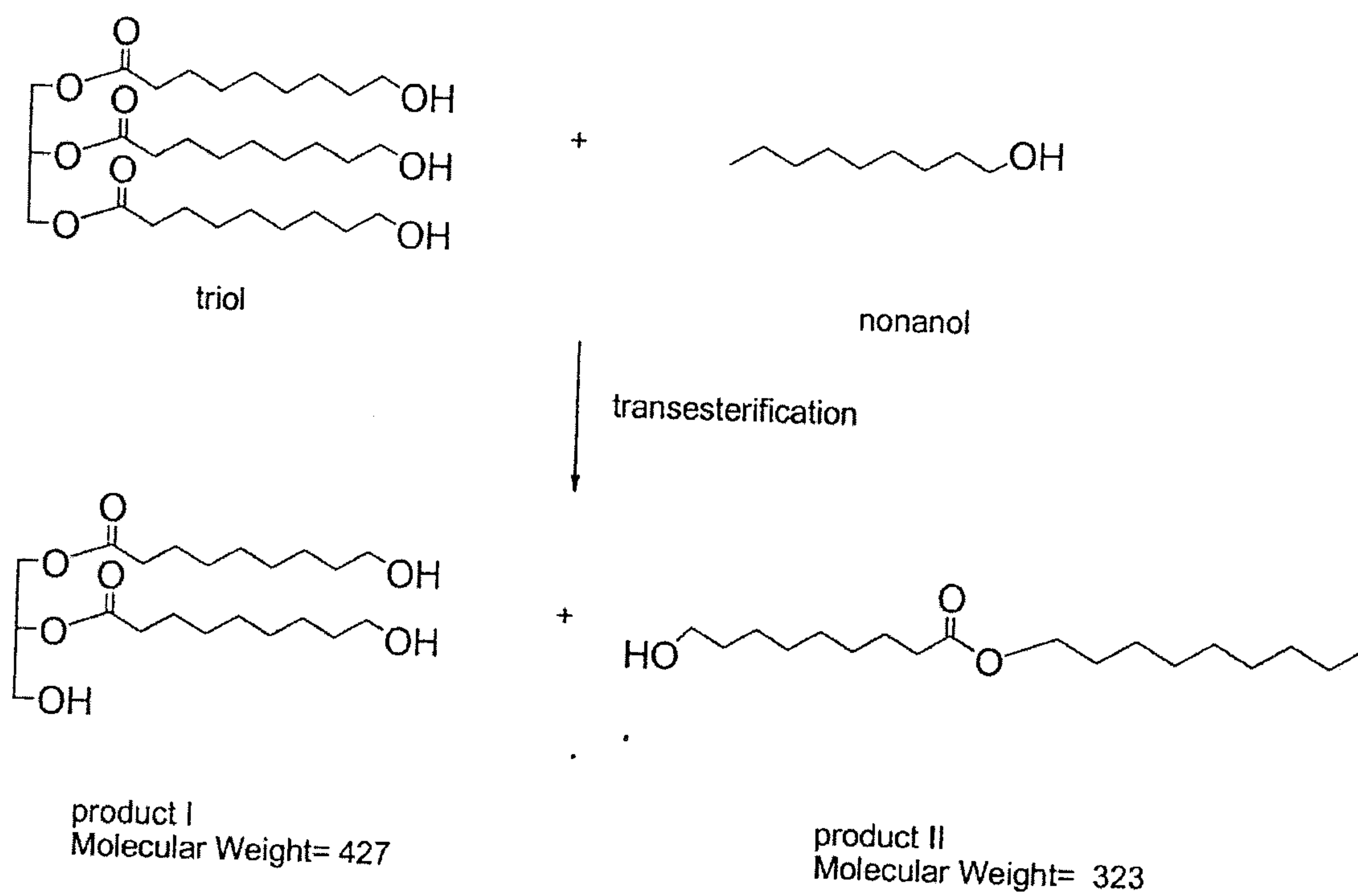
Figure 15: Transesterification Reaction of Triol

Figure 16: MS of Transesterified Product

Product I: Transesterified Product with Molecular Weight 427.2
Product II: Transesterified Product with Molecular Weight 323.3

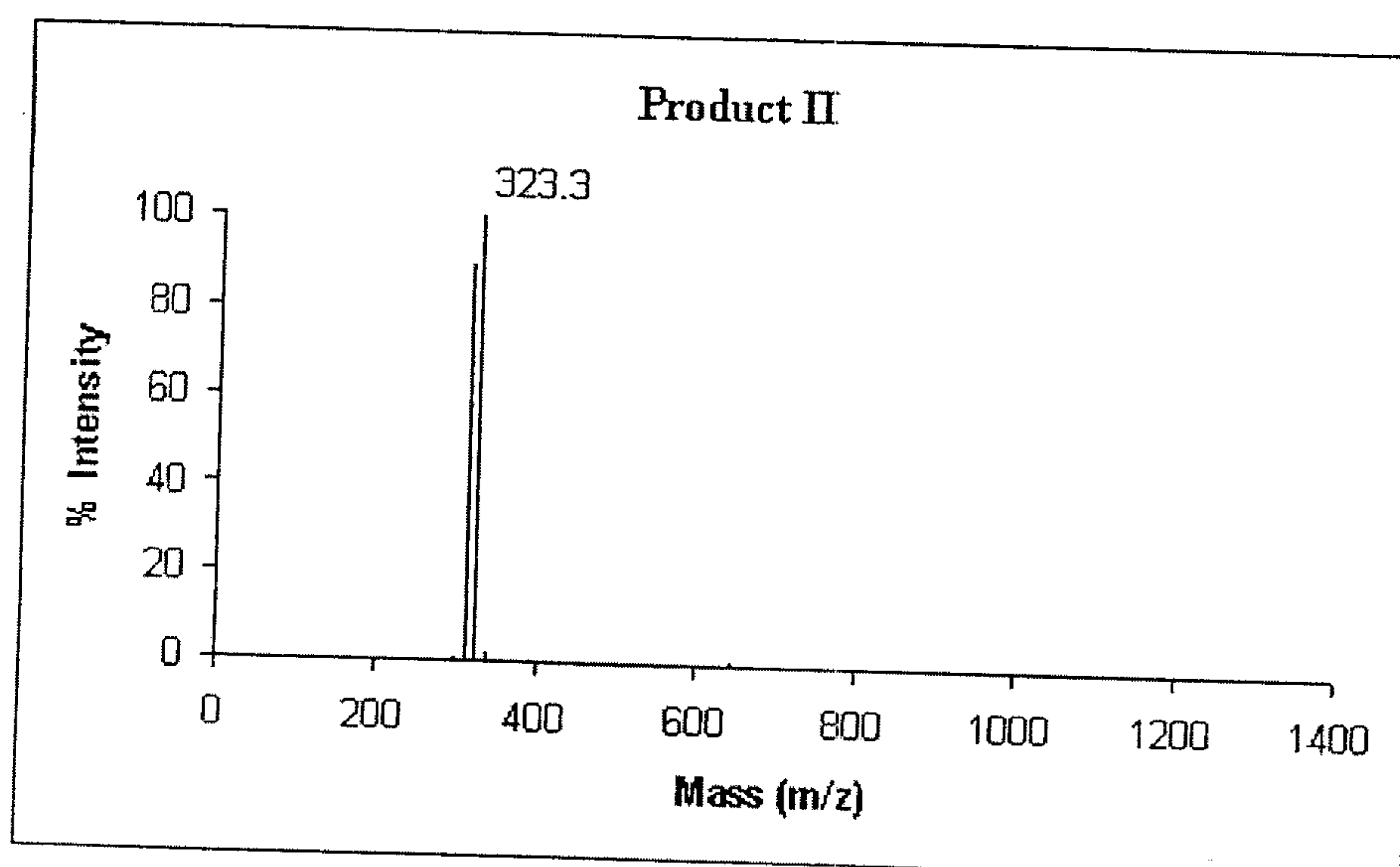
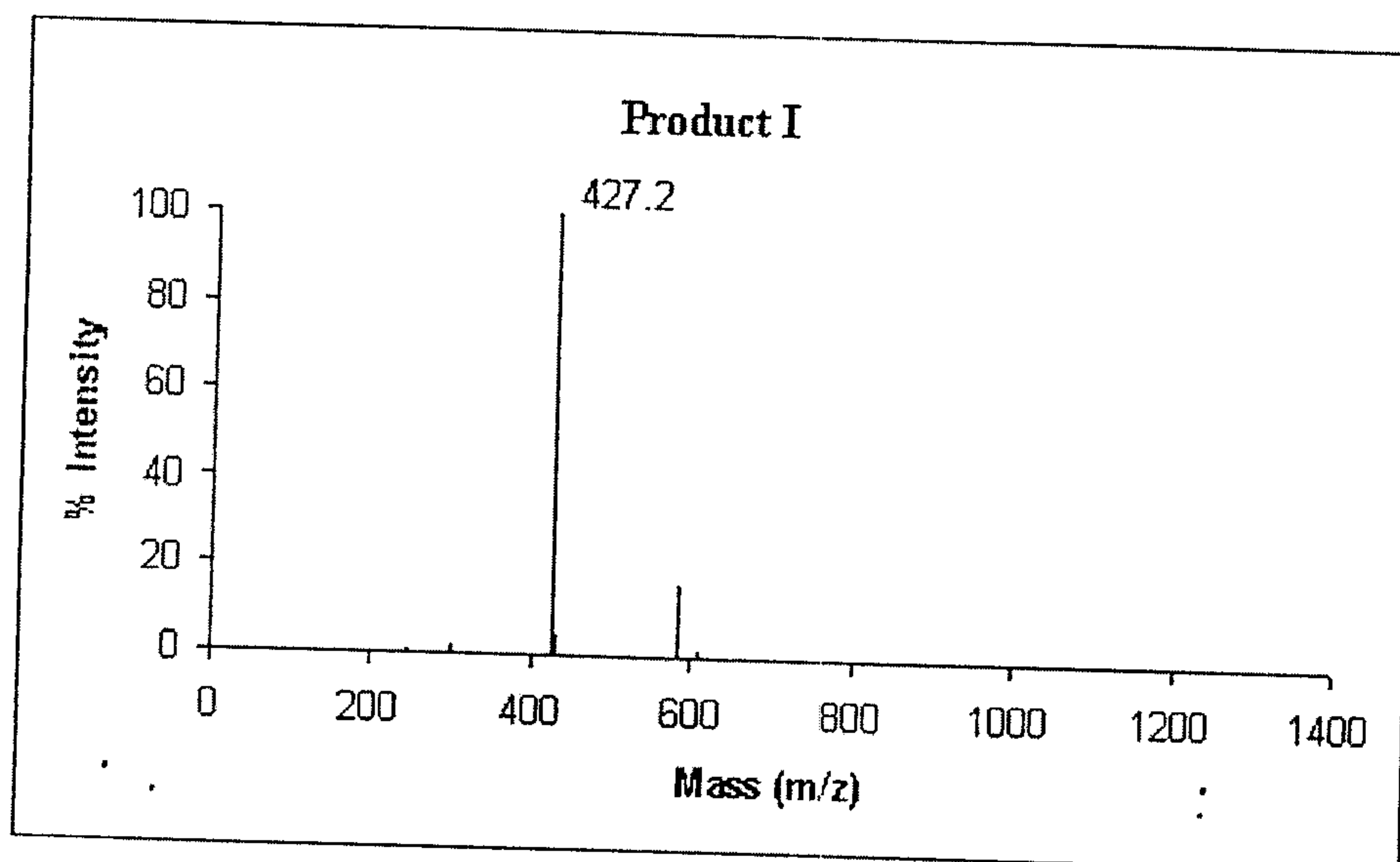


Figure 17:

GC graph of Canola based reaction products, which was ozonized at 0°C with air as a supply gas for 8h. (a) before distillation. (b) after distillation.

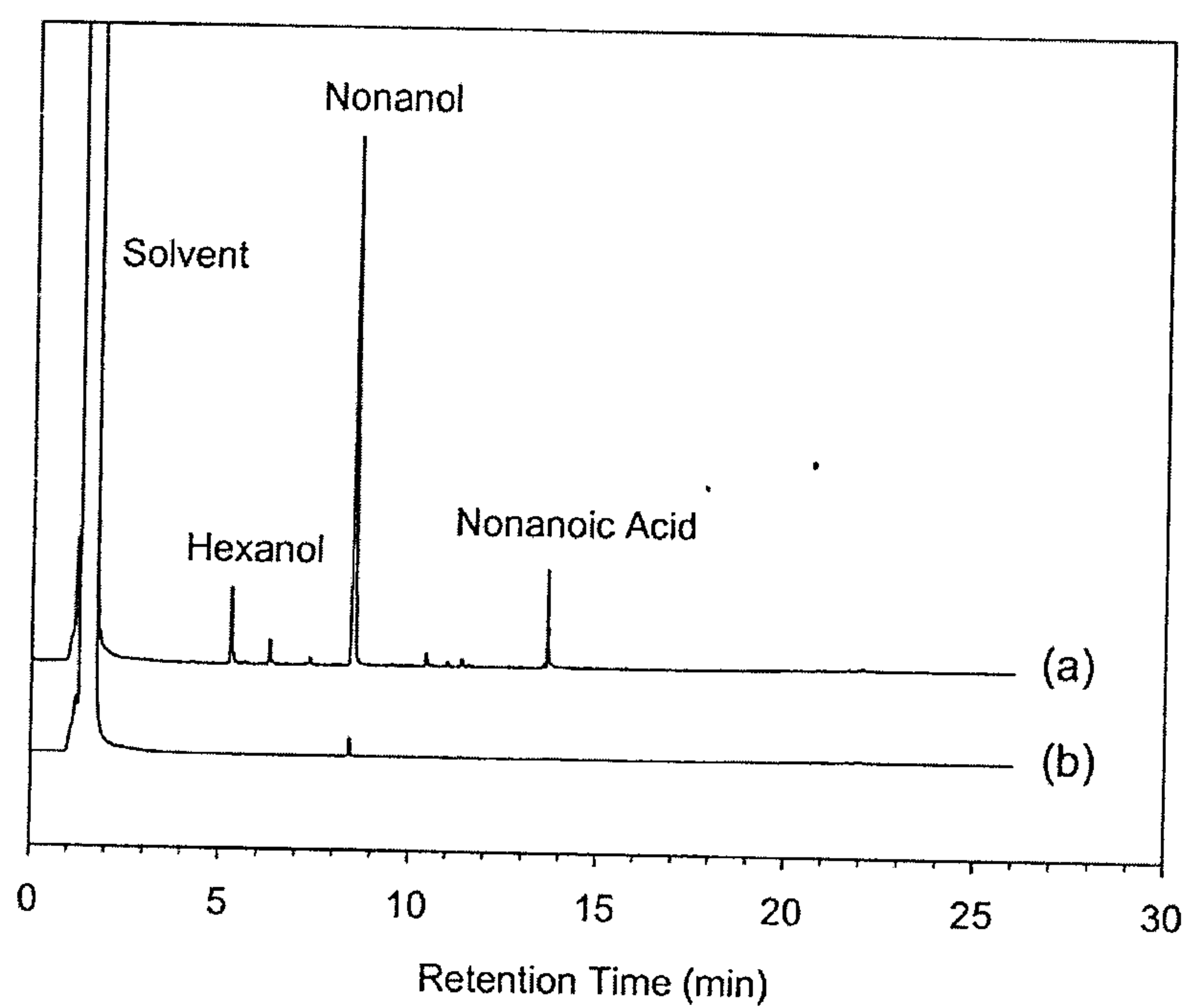


Figure 18: FTIR spectra of: (a) Canola oil (b) Flax oil (c) Canola-air polyol (d) Flax-air polyol (e) Canola-oxygen polyol.

Figure 18(a): FTIR spectra in the range 400-4000 cm^{-1} .

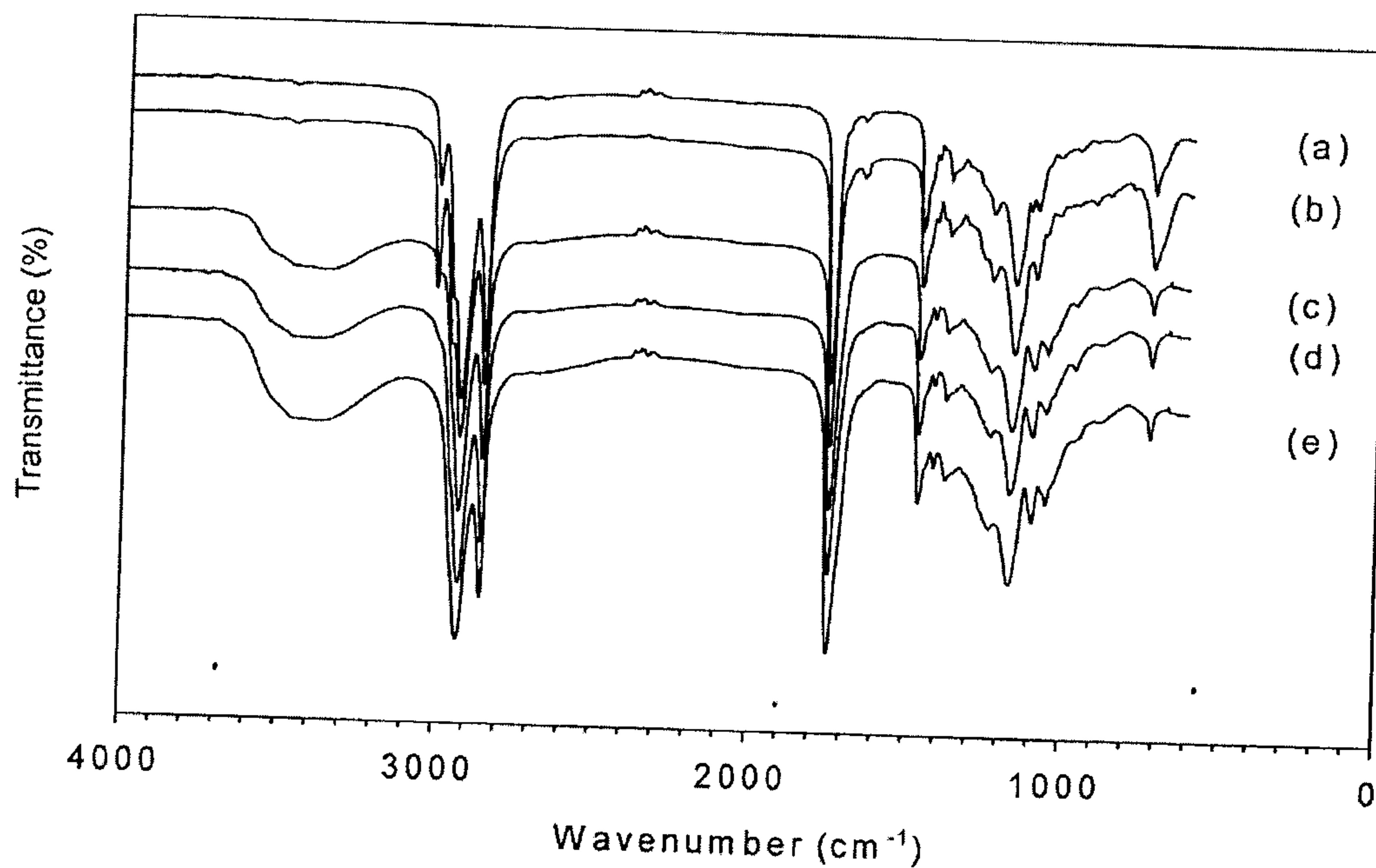


Figure 18(b): Enlargement of the FTIR band at 1650 cm^{-1} characteristic of C=C double bond.

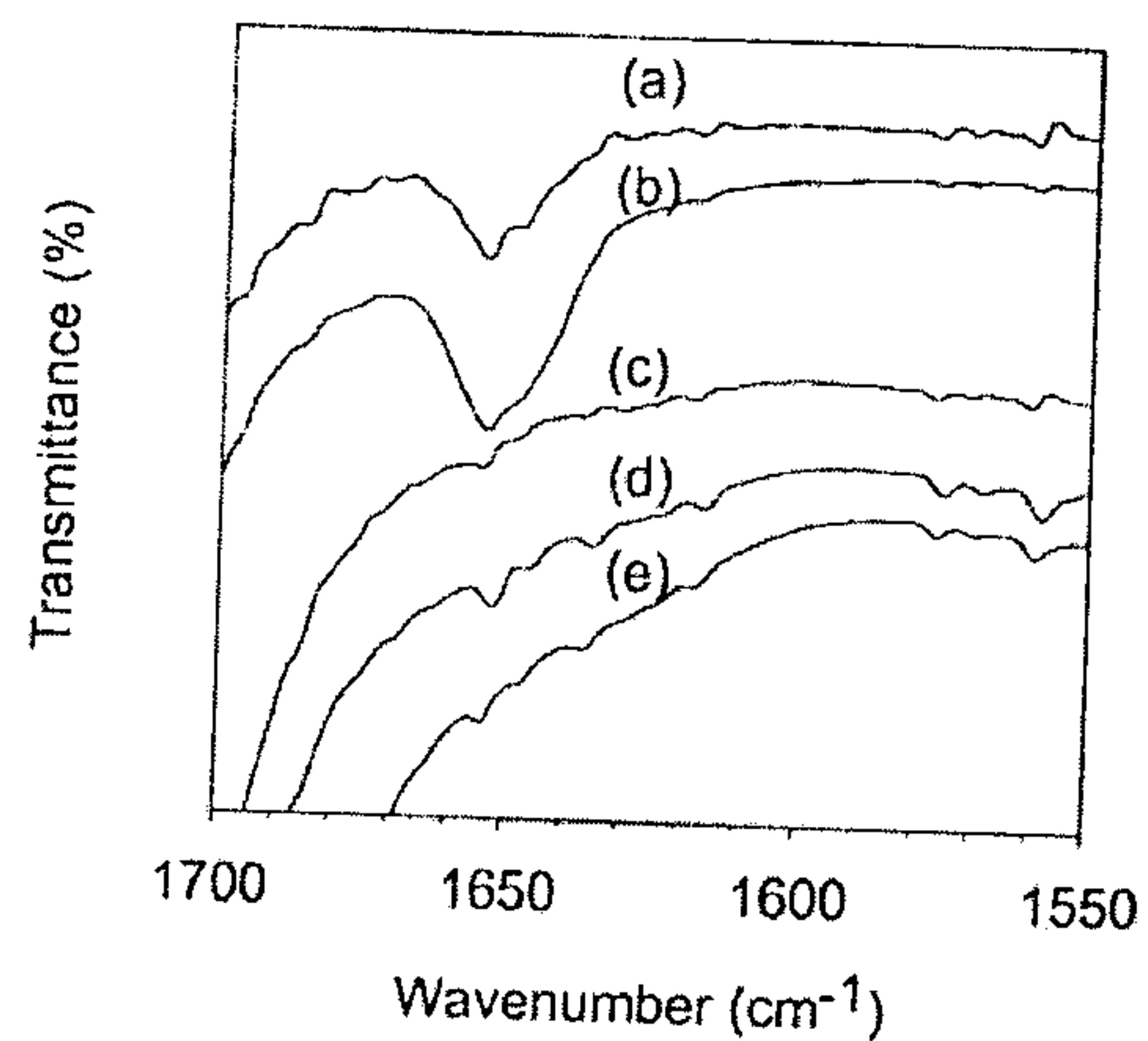


Figure 18(c): Enlargement of the FTIR band at 3006 cm^{-1} characteristic of unsaturated C-H stretches.

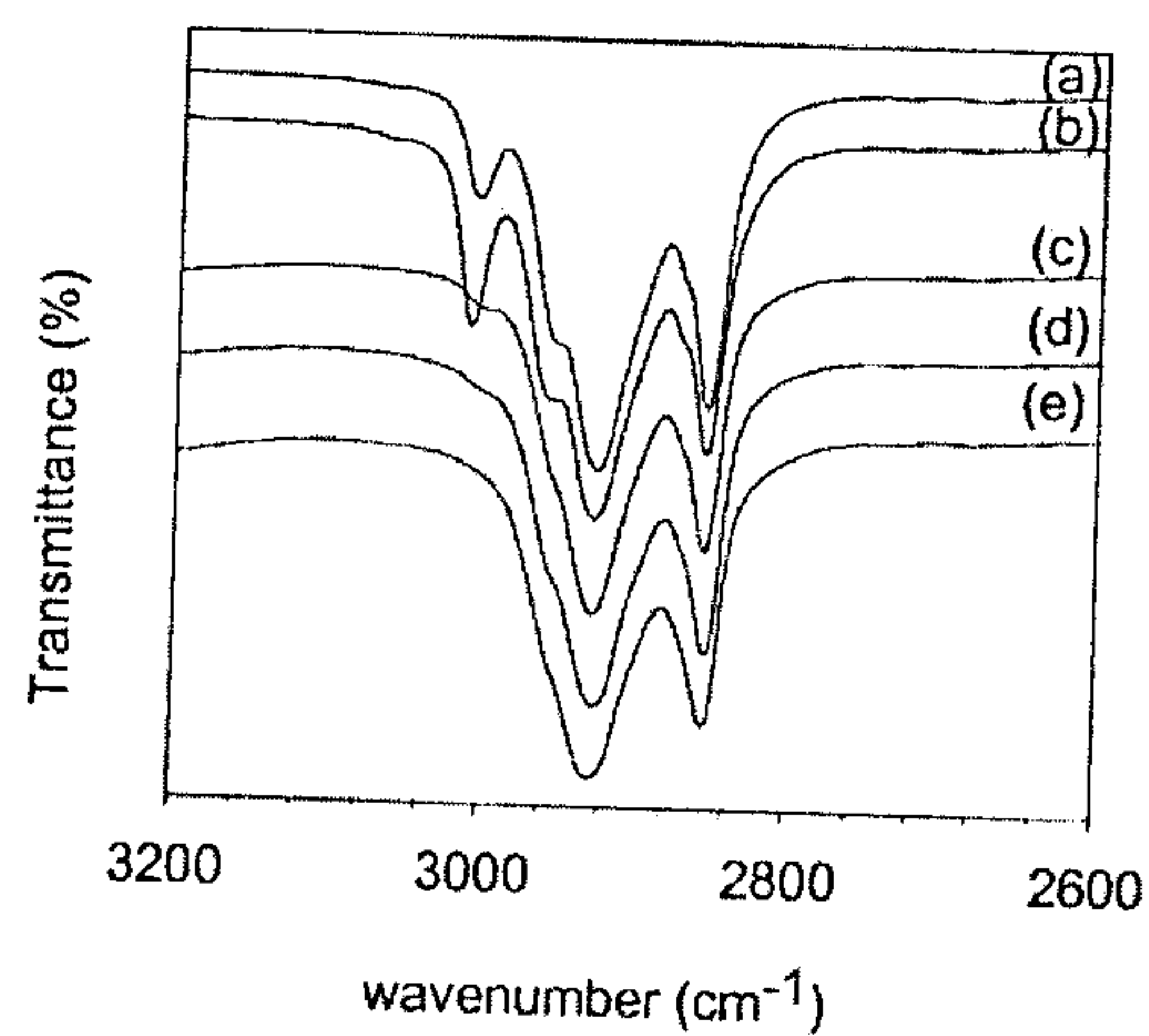


Figure 19: HPLC chromatography of Canola-air polyol, ozonized for 8h at 0°C.

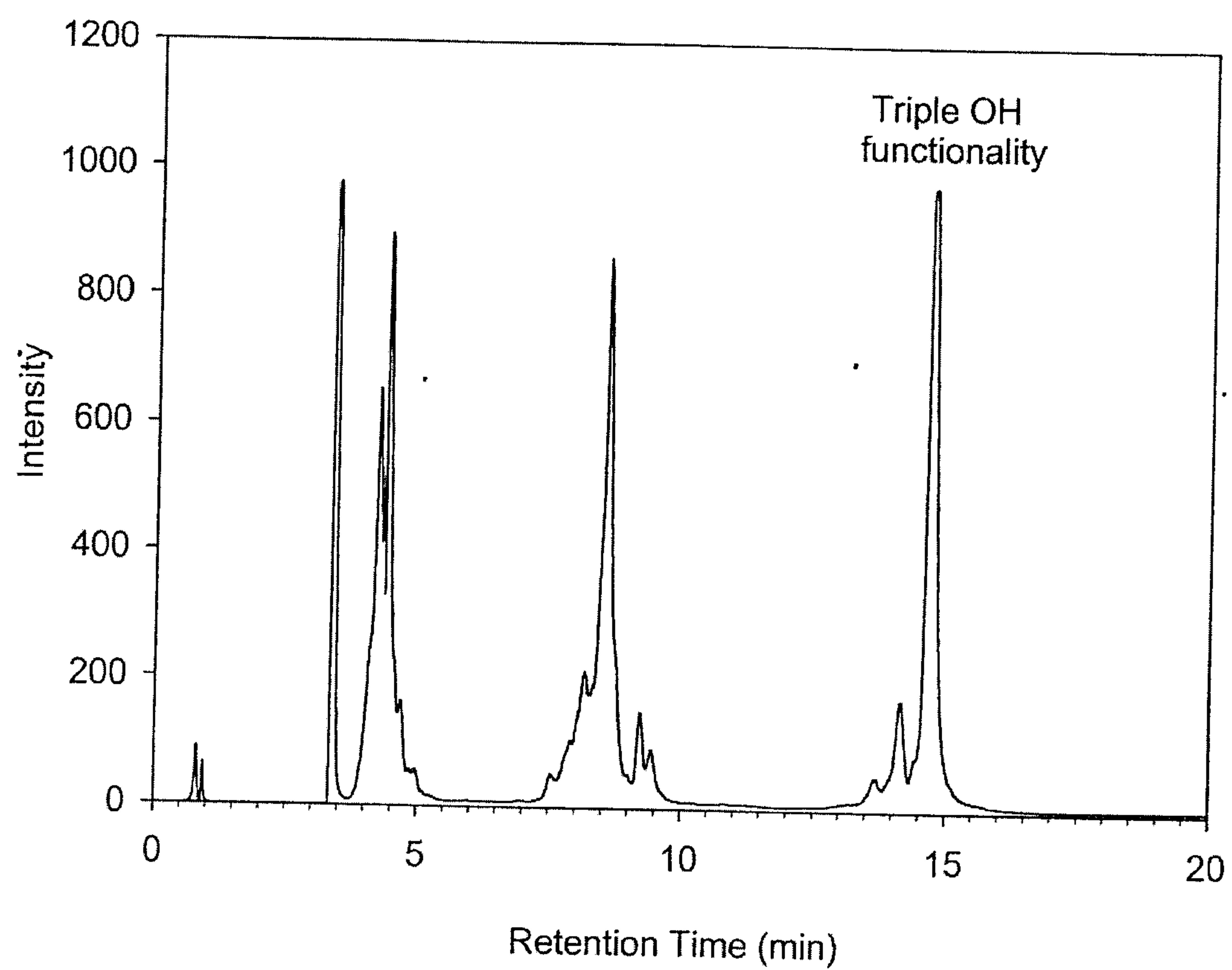


Figure 20a: DSC crystallization curves of:

- (a) Canola oil
- (b) Flax oil
- (c) Canola-air polyol (d) Flax-air polyol
- (e) Canola-oxygen polyol and
- (f) Hydrogenated Canola oil

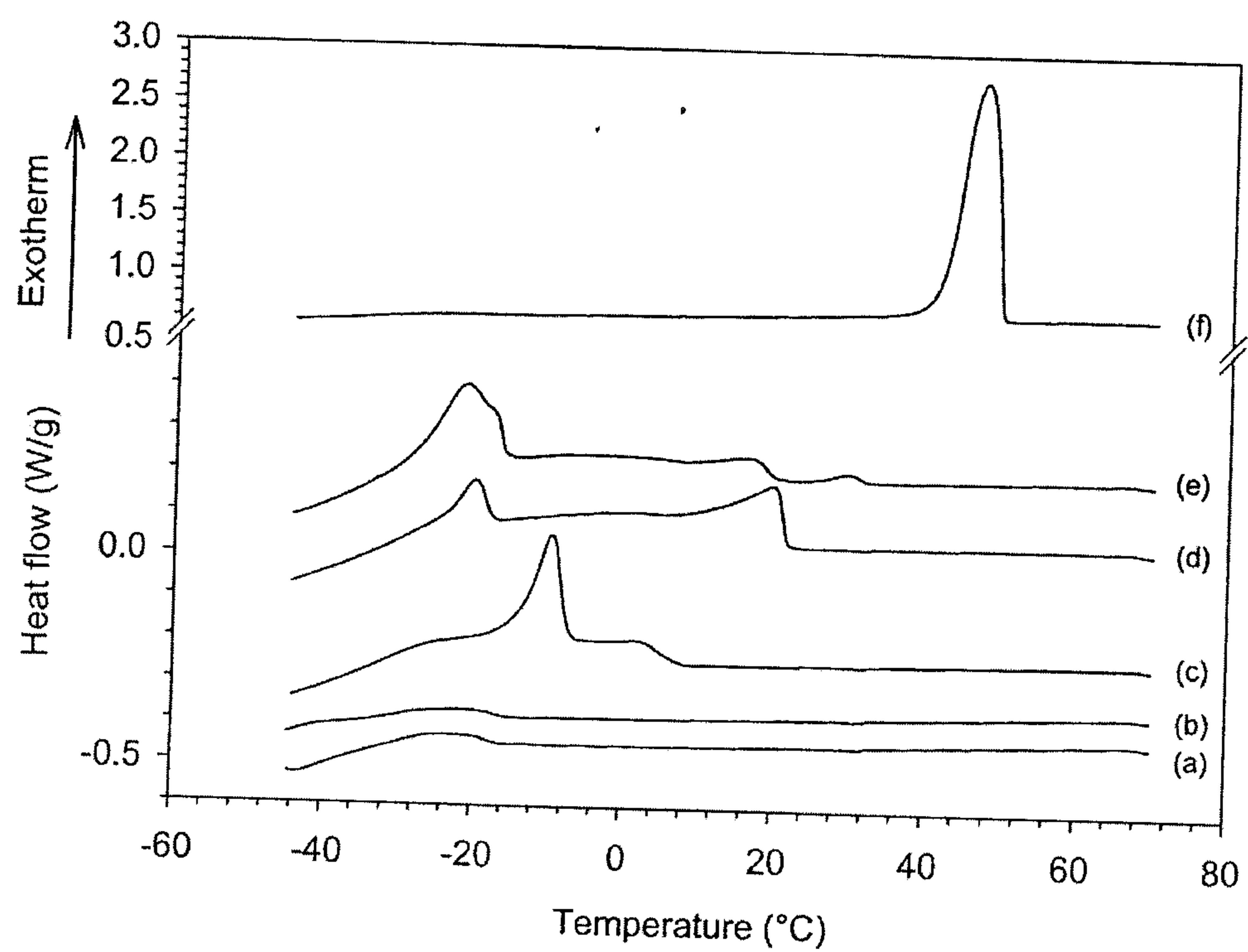


Figure 20b: DSC melting curves of:

- (a) Canola oil
- (b) Flax oil
- (c) Canola-air polyol
- (d) Flax-air polyol
- (e) Canola-oxygen polyol and
- (f) Hydrogenated Canola oil.

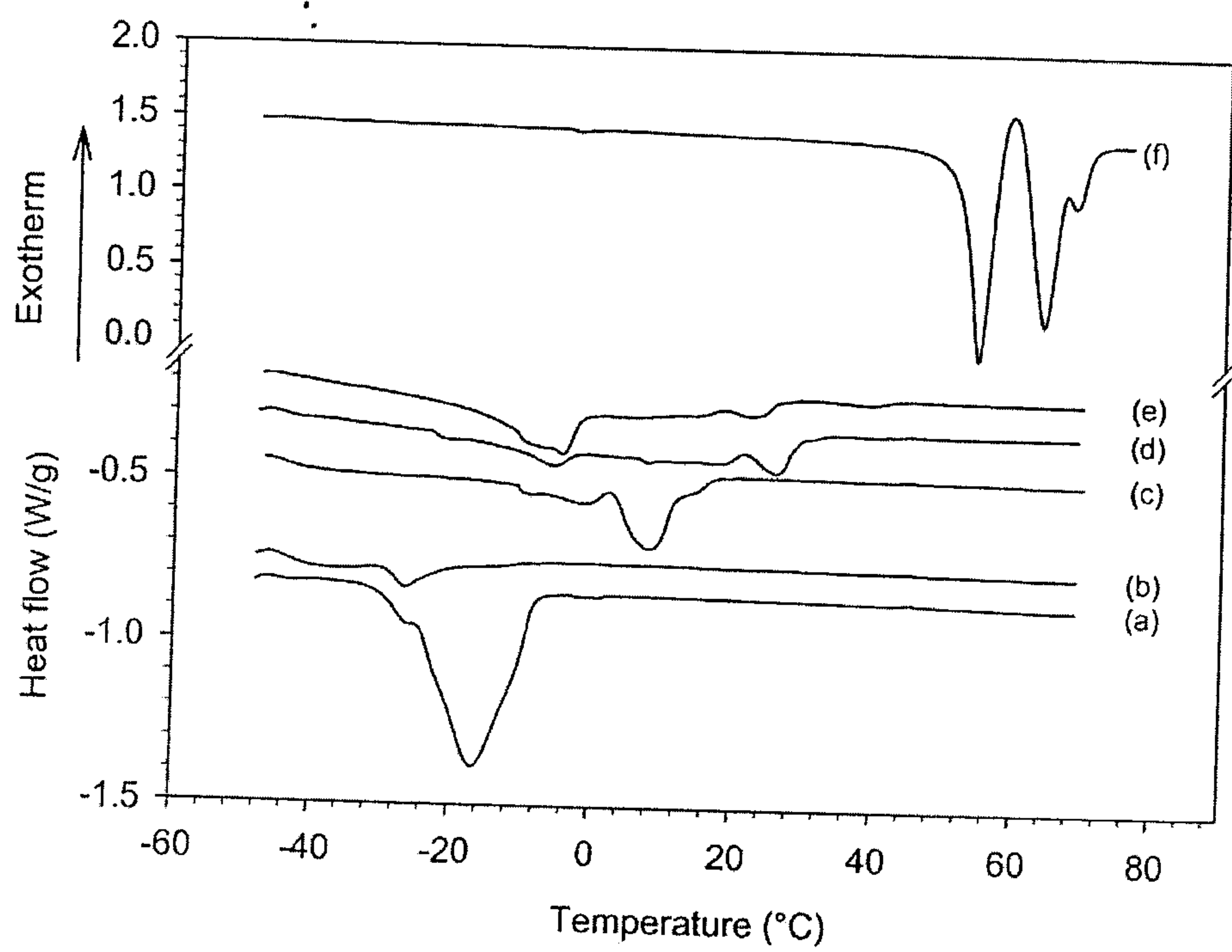


Figure 21: Viscosity of: (a) Flax oil (b) Canola oil, (c) Canola-air polyol, (d) Flax-air polyol, (e) Canola-oxygen polyol.

Figure 21(a): Viscosity as a function of time.

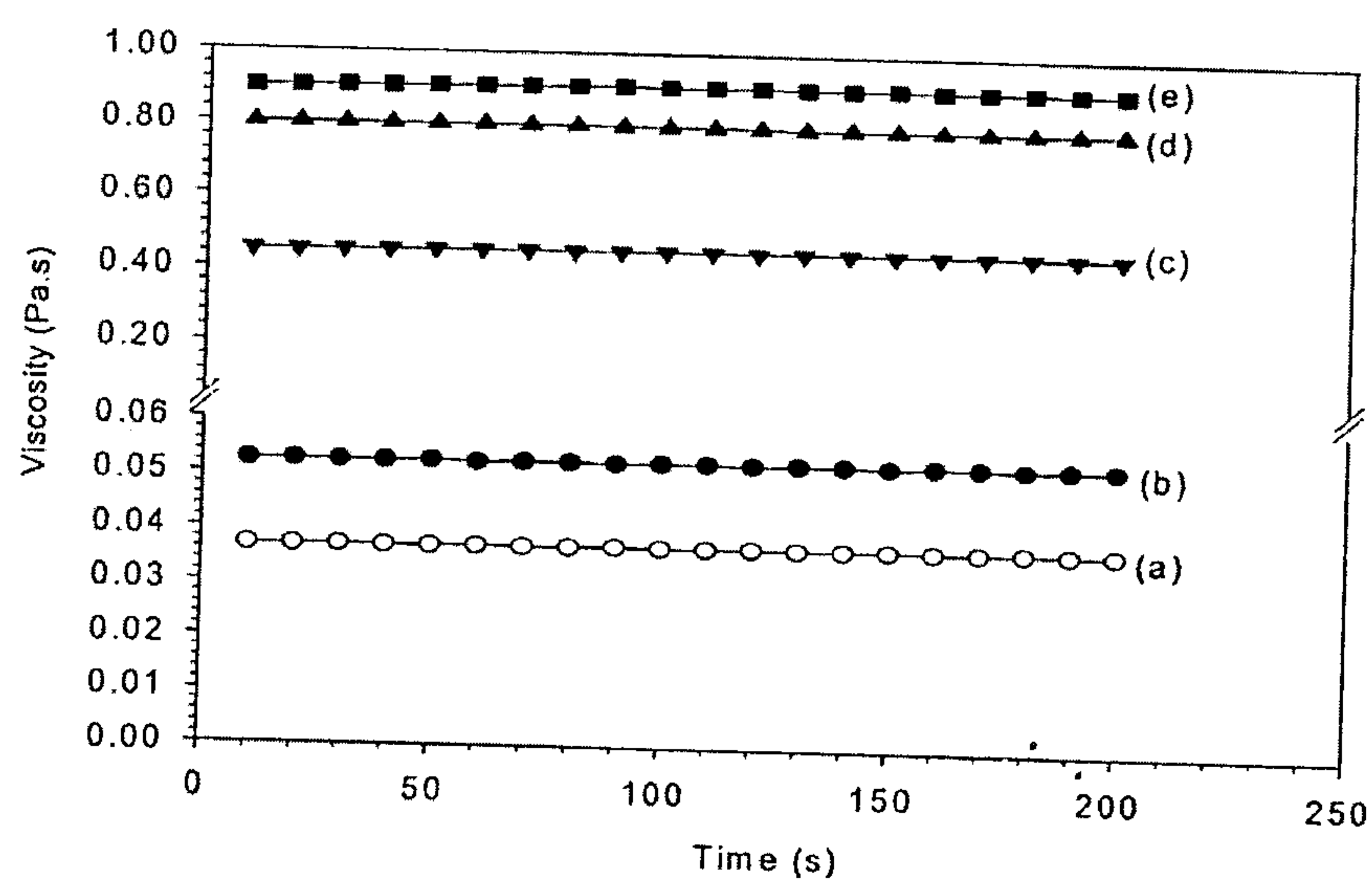


Figure 21(b): Viscosity as a function of temperature.

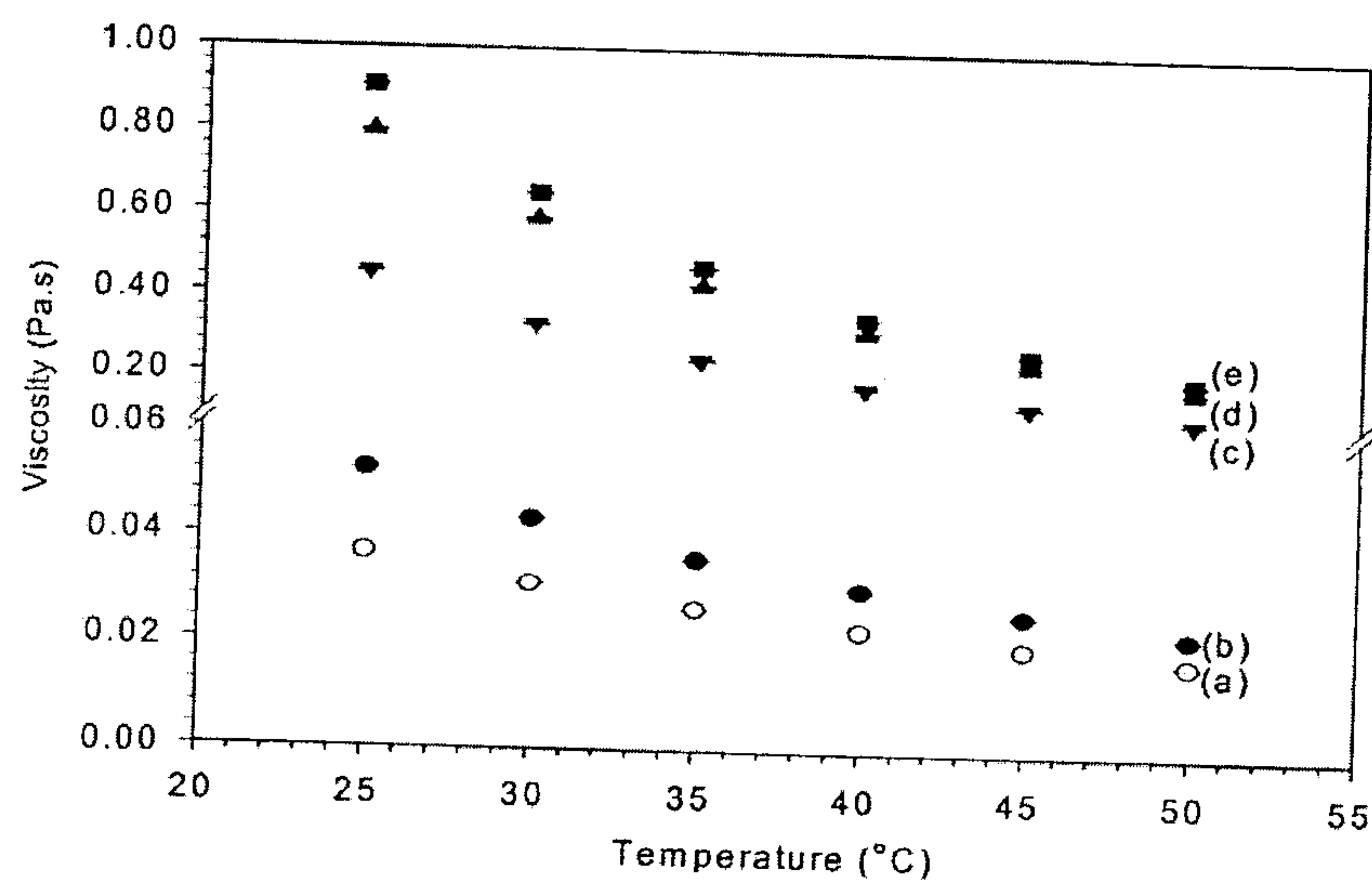


Figure 22: FTIR spectra of elastomers with OH/NCO molar ratio 1.0

(a) canola oil based polyurethane (COBPU); (b) flax oil based polyurethane (FOBPU); and (c) soybean oil based polyurethane (SOBPU).

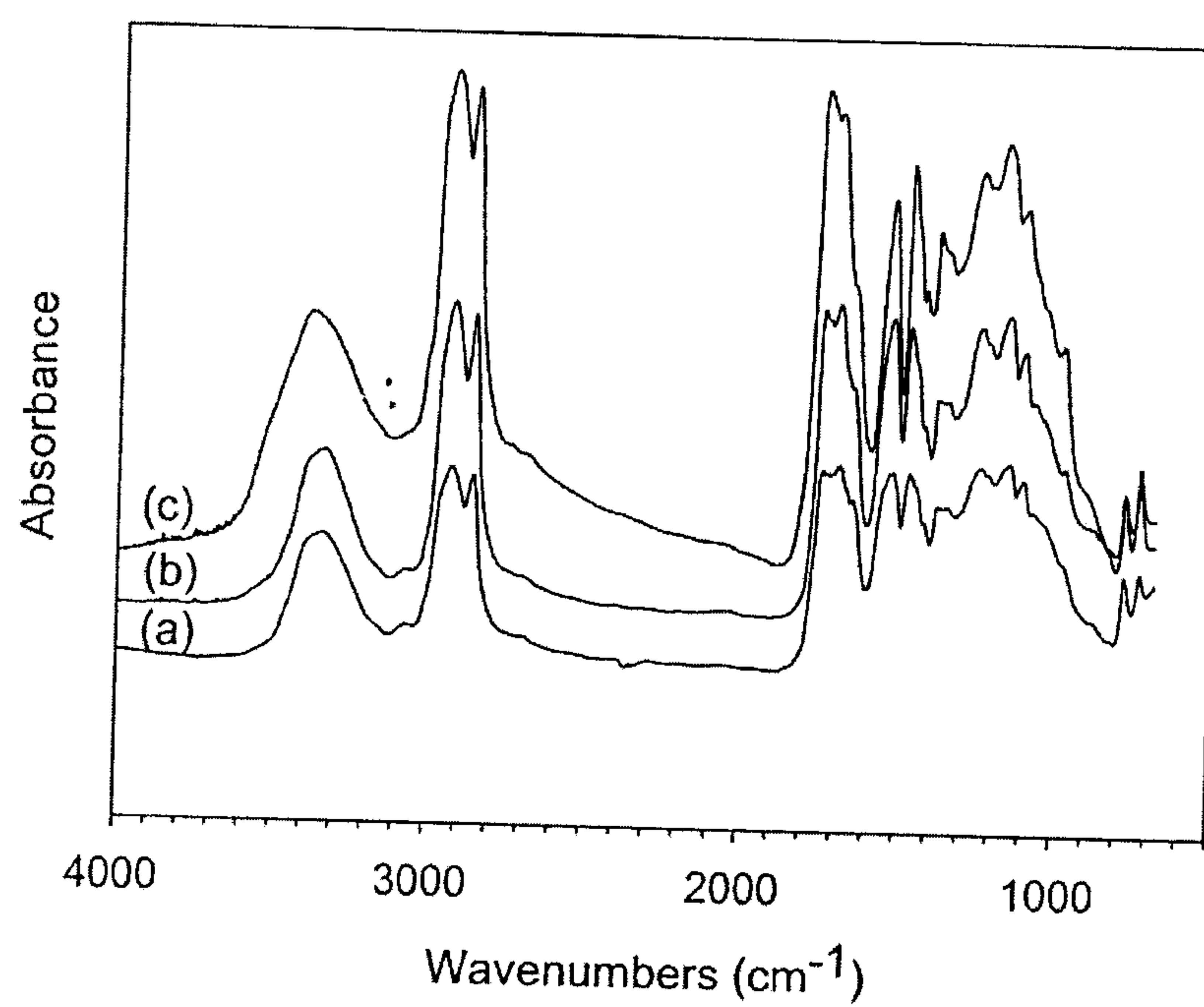


Figure 23: Reversing heat flow vs. temperature of elastomers with OH/NCO molar ratio 1.0. (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU).

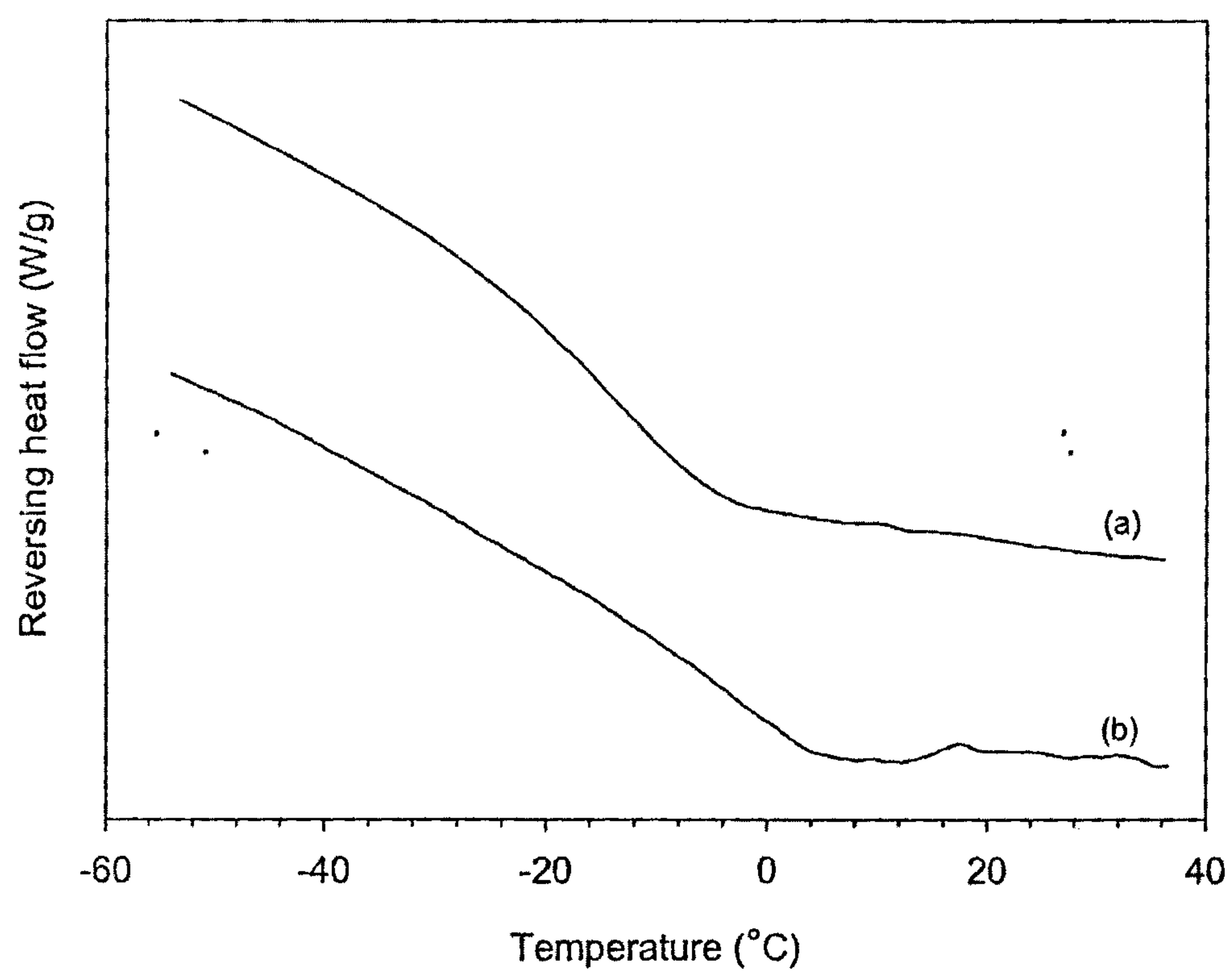


Figure 24: Thermomechanical analysis curves of elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU).

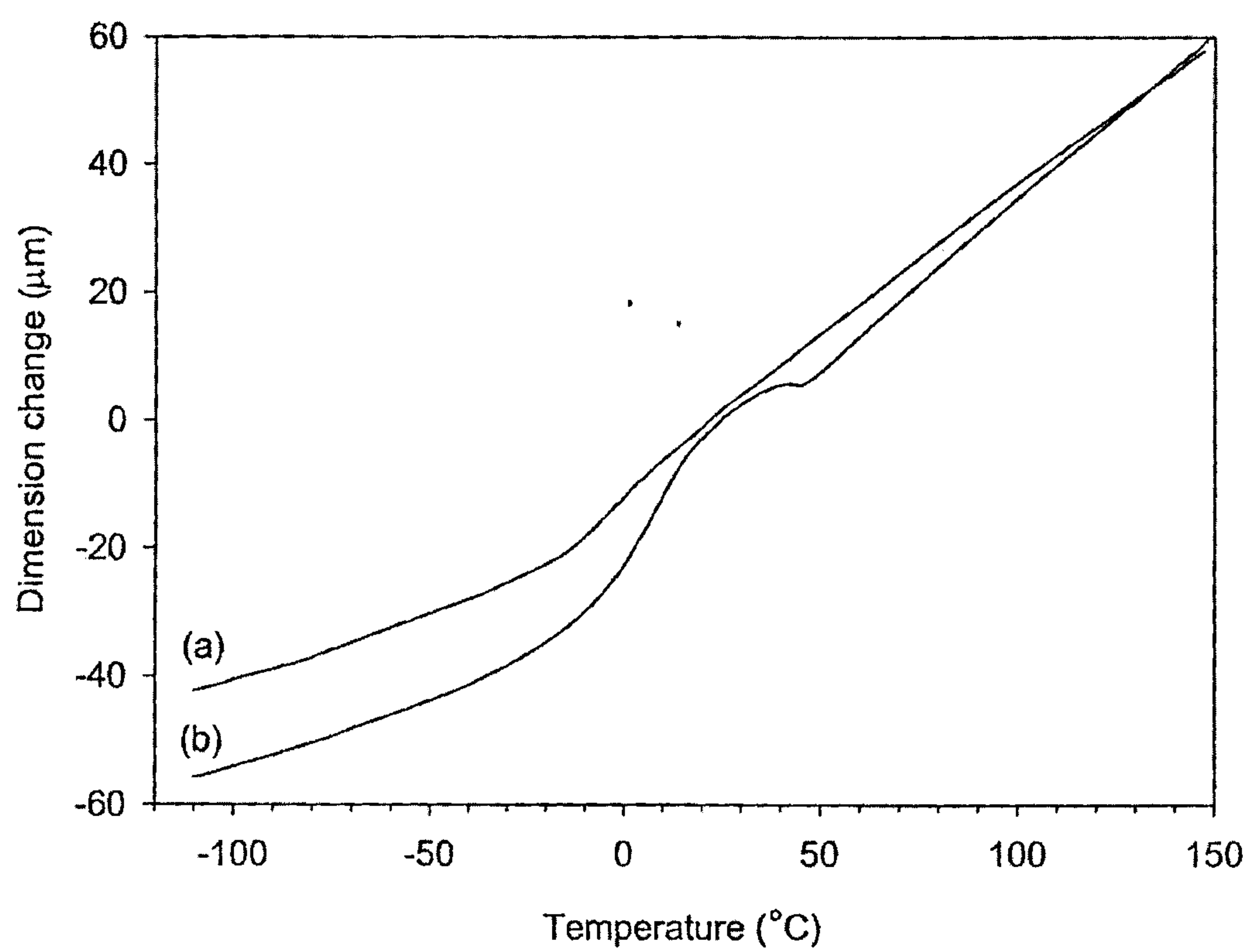


Figure 25: Storage moduli elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU).

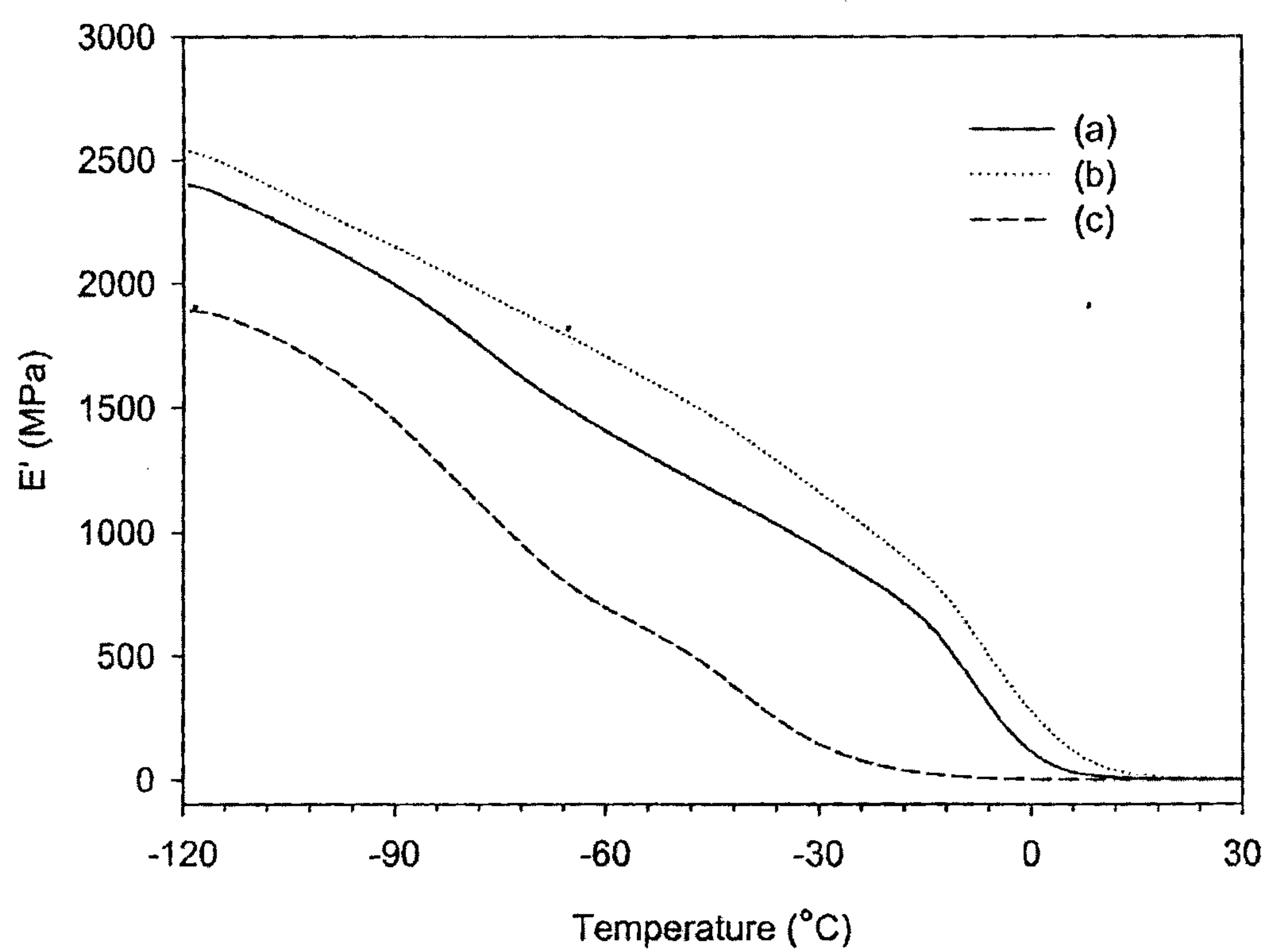


Figure 26(a): TGA of elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU).

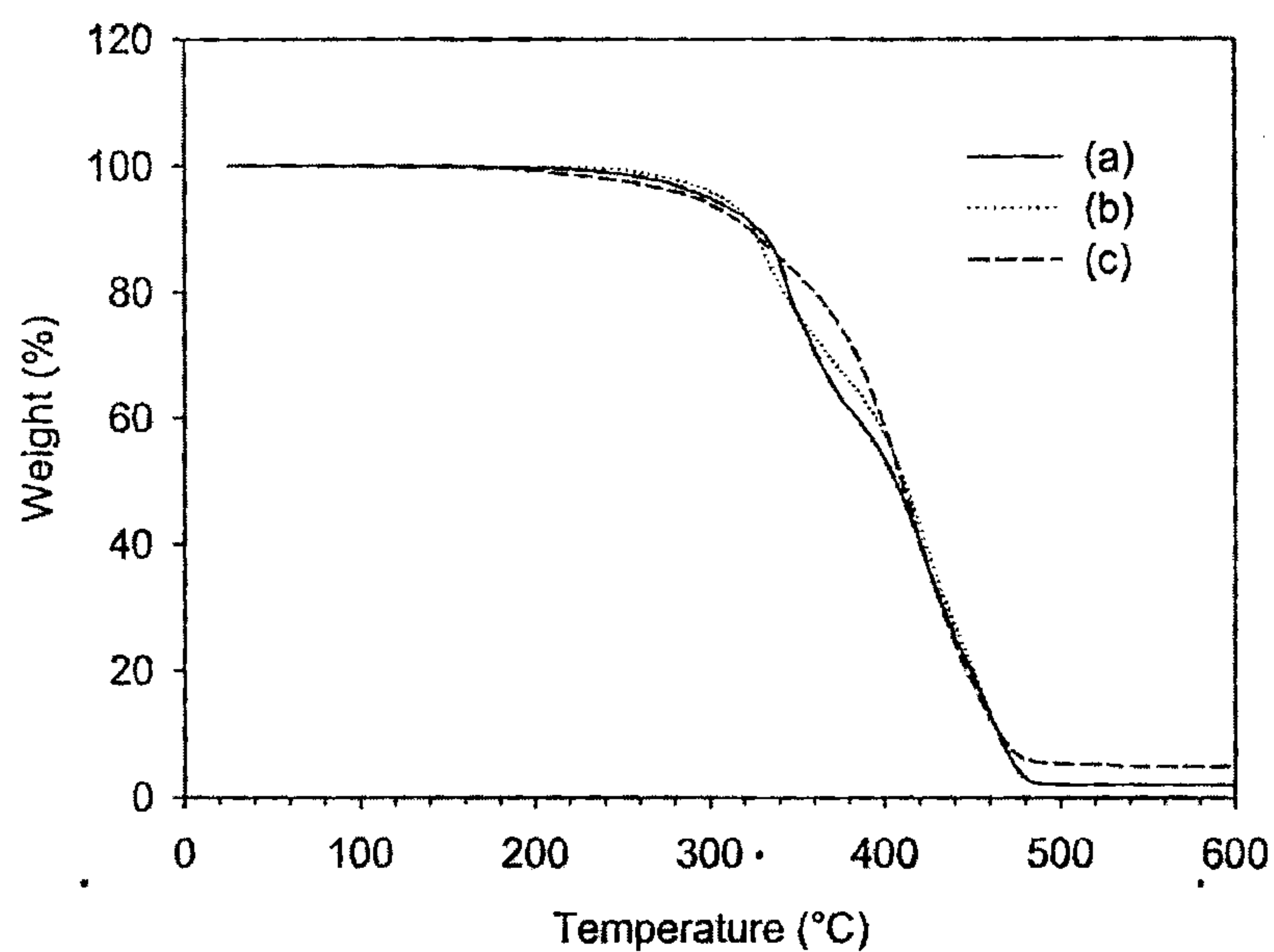


Figure 26(b): Derivative TGA curves elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU) (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU).

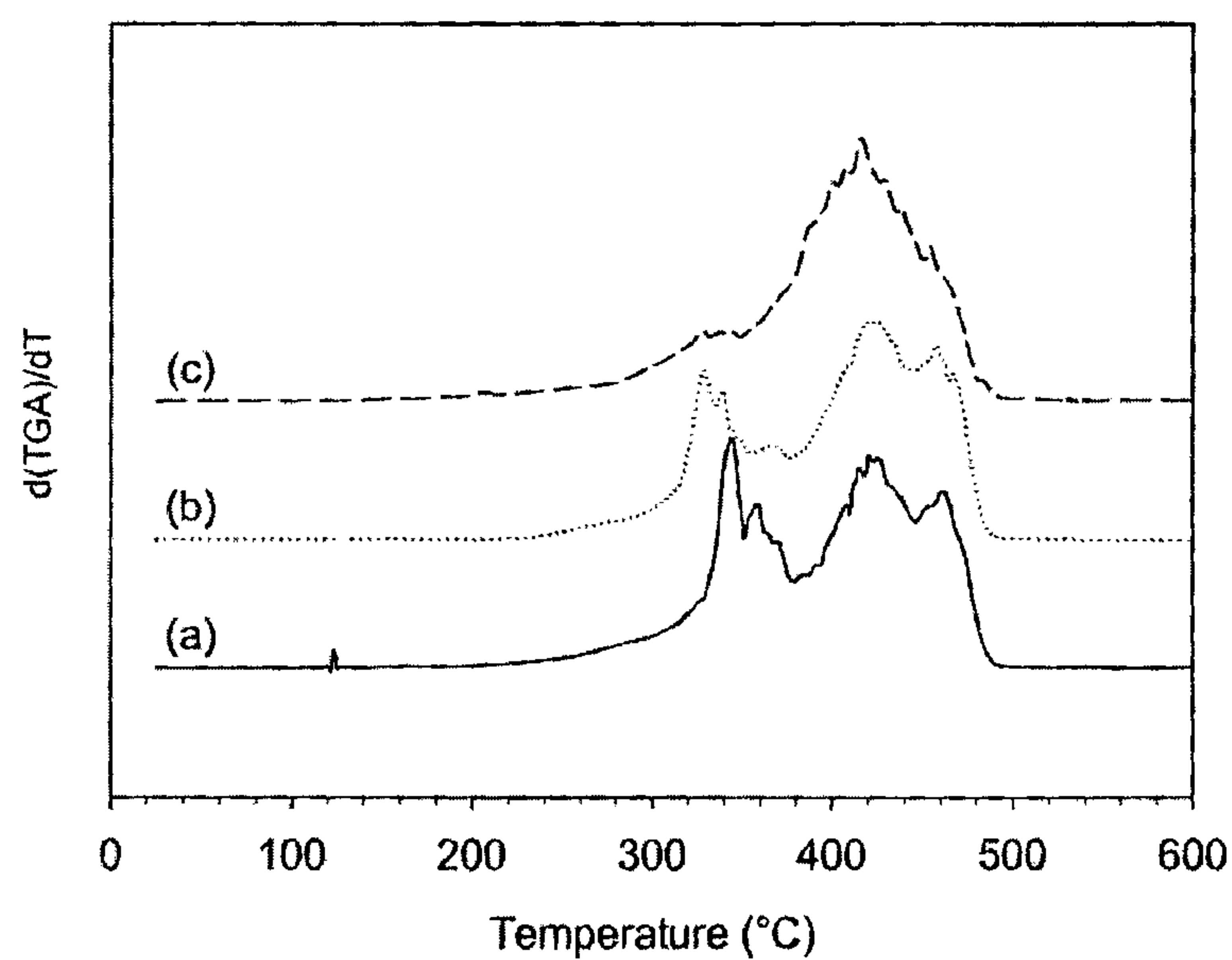


Figure 27: Nominal stress-strain of elastomers with OH/NCO molar ratio 1.0 (a) canola oil based polyurethane (COBPU), (b) flax oil based polyurethane (FOBPU) and (c) soybean oil based polyurethane (SOBPU).

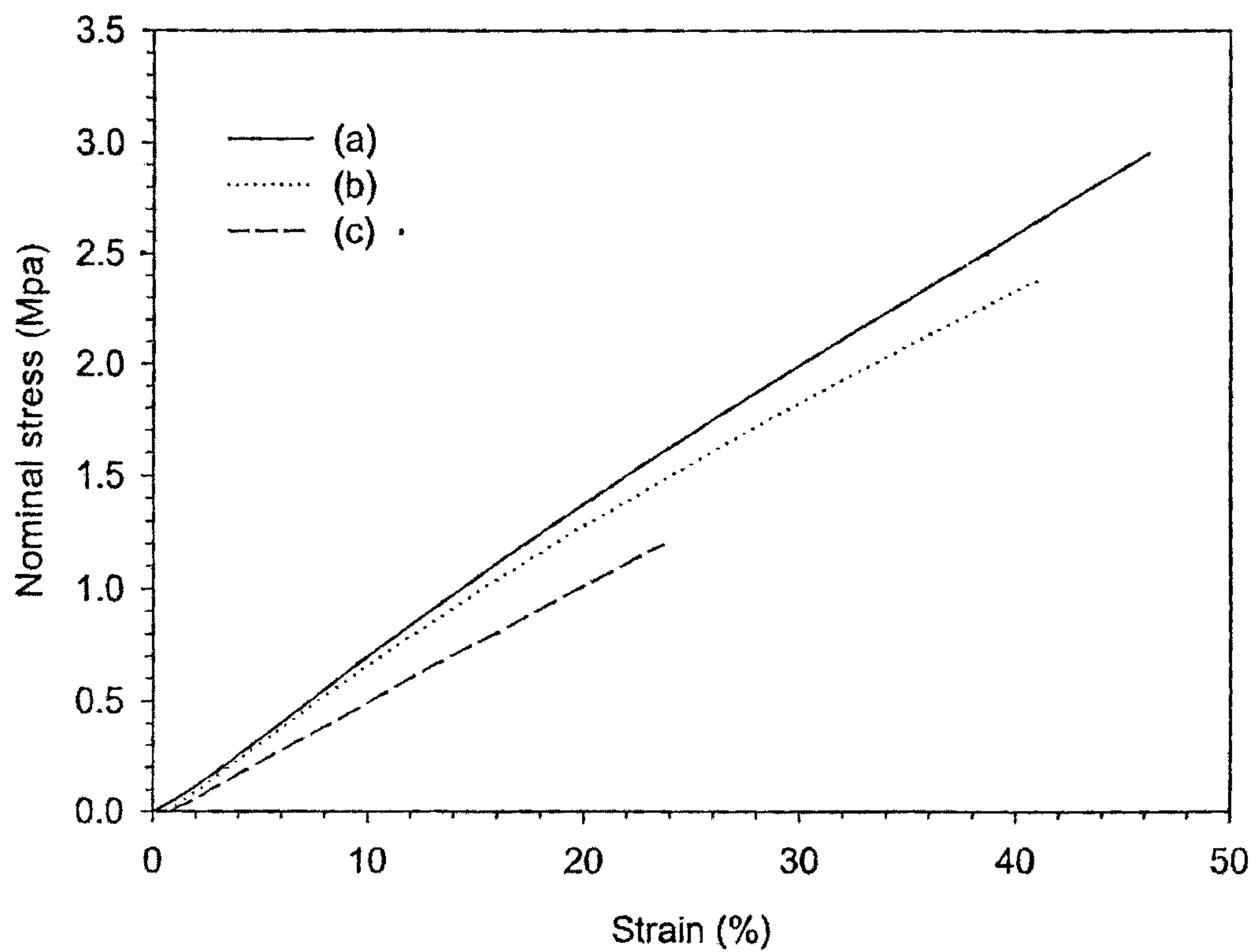


Figure 28: FTIR spectra of polyurethane foams. (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

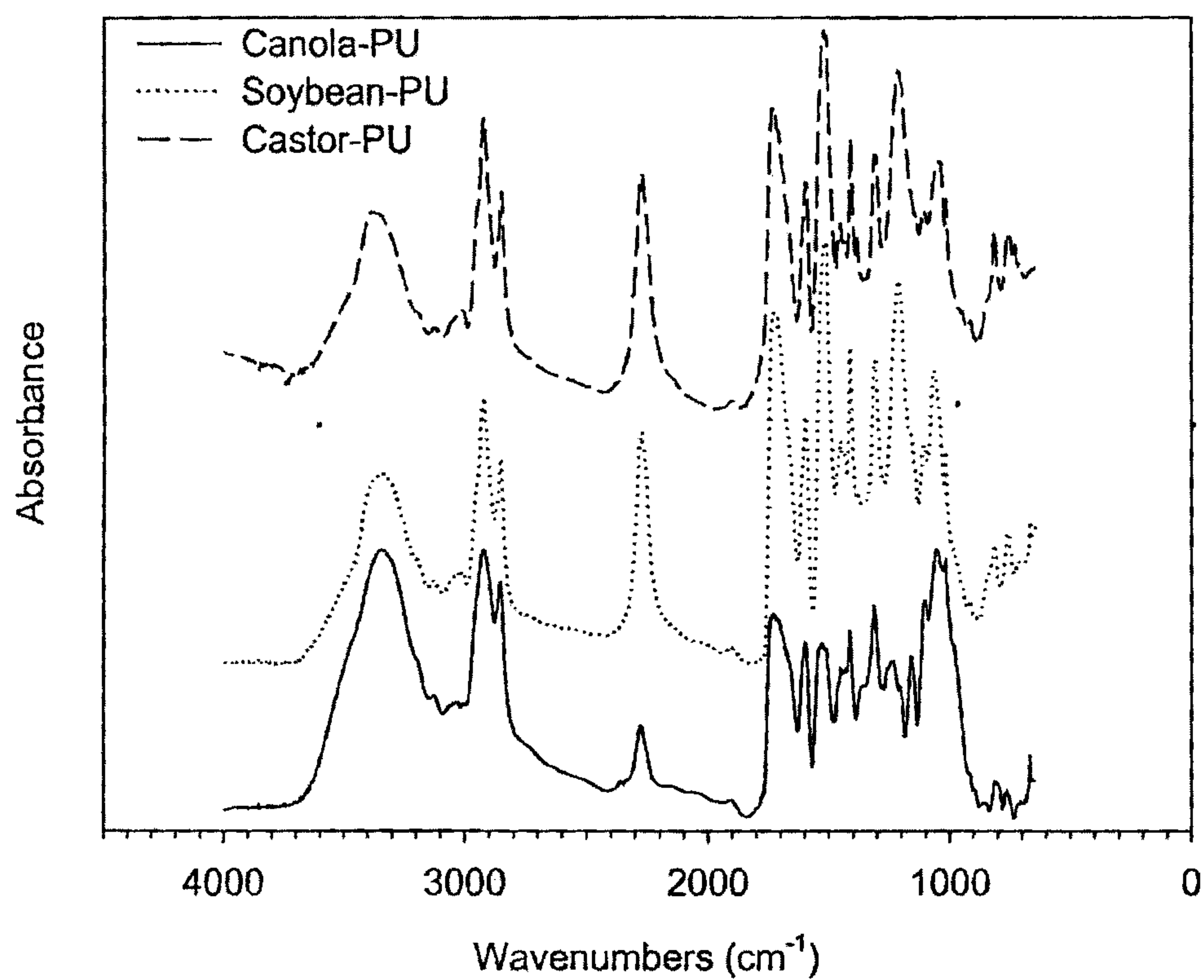


Figure 29(a): Storage moduli of polyurethane foams. Insert: first derivatives relative to temperature of storage moduli. (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

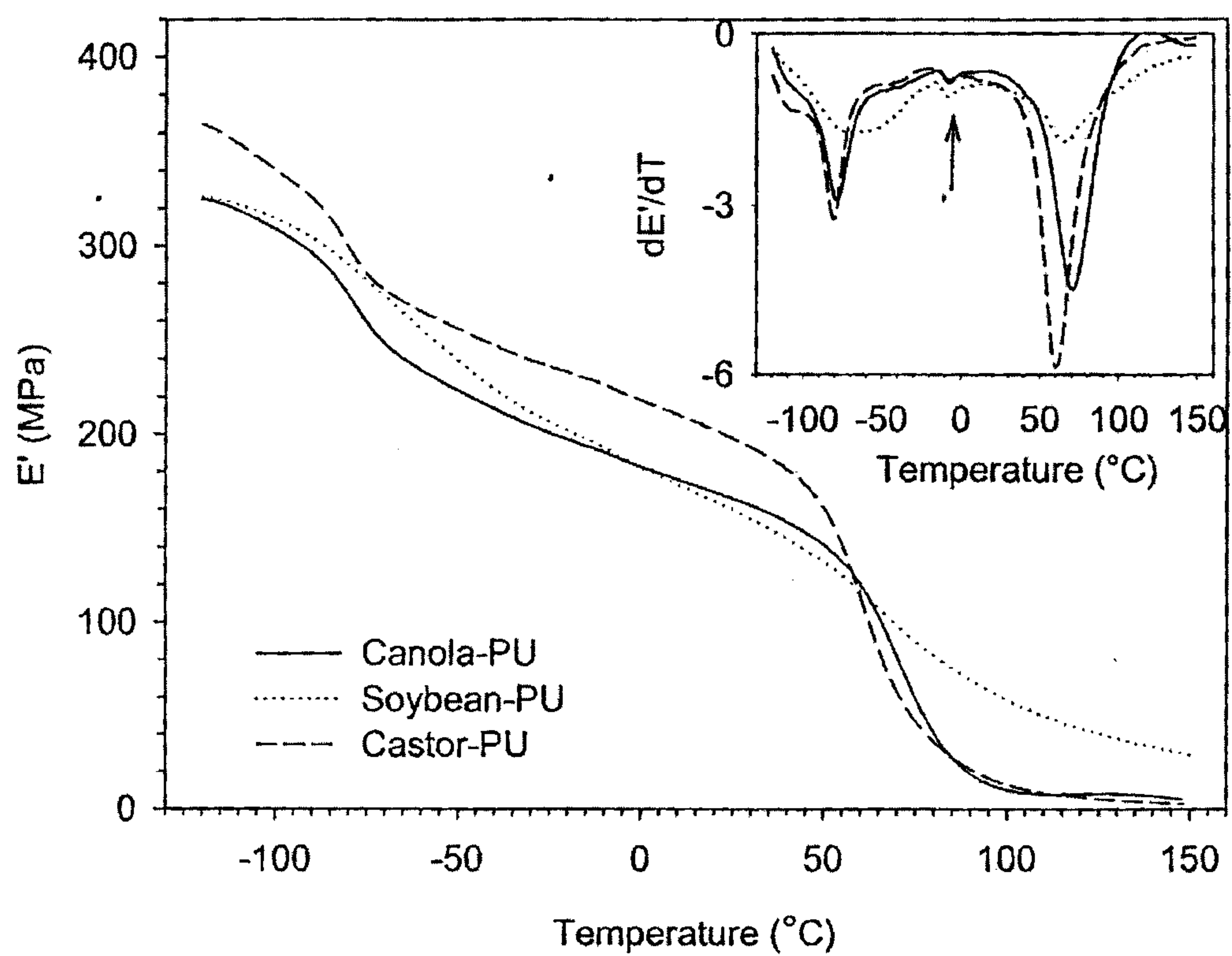


Figure 29(b): Loss moduli. (—) Canola oil based polyurethane (Canola-PU), (.....) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

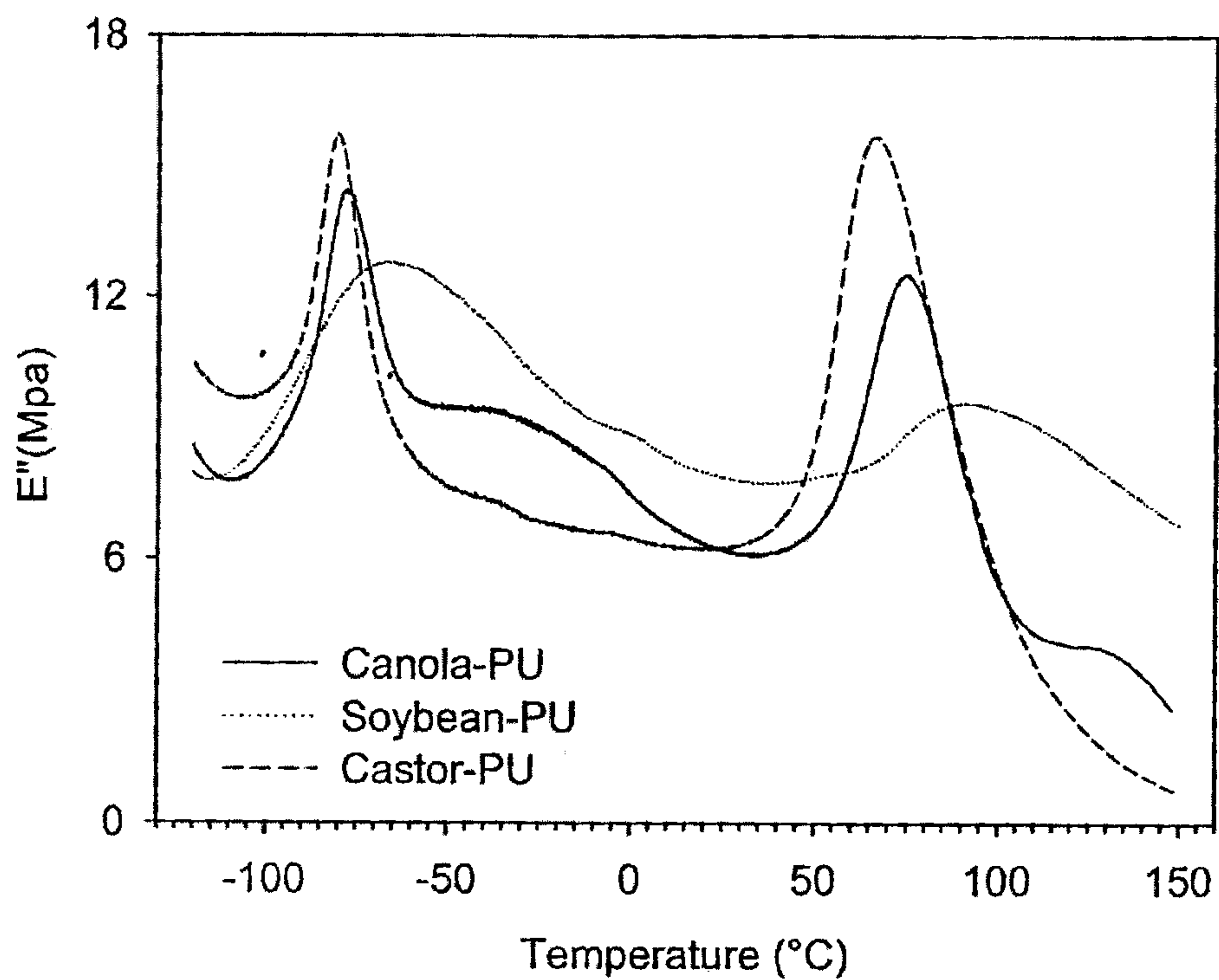


Figure 29(c): Tan δ of polyurethane foams. (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

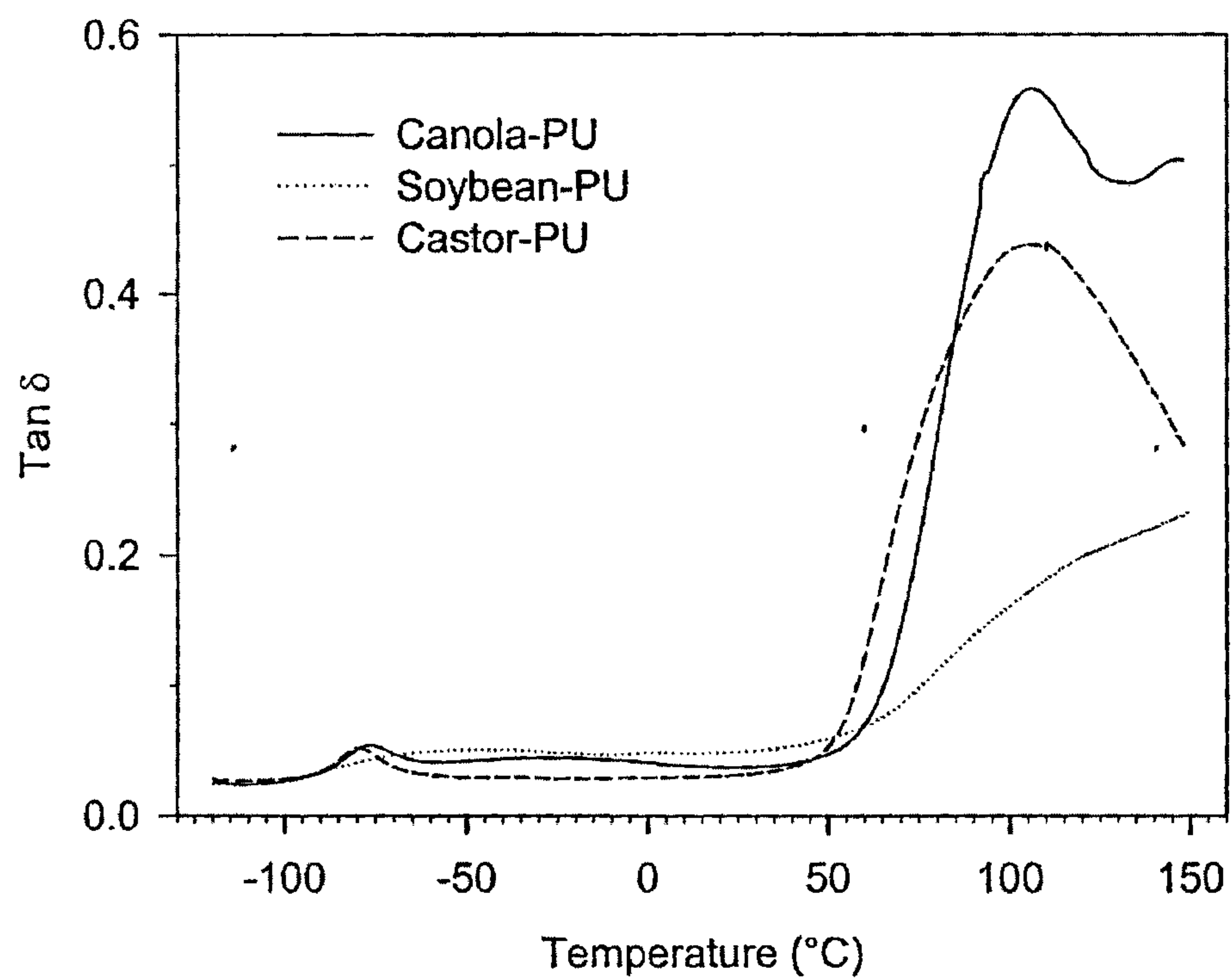


Figure 30(a): TGA curves of polyurethane foams in nitrogen. (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

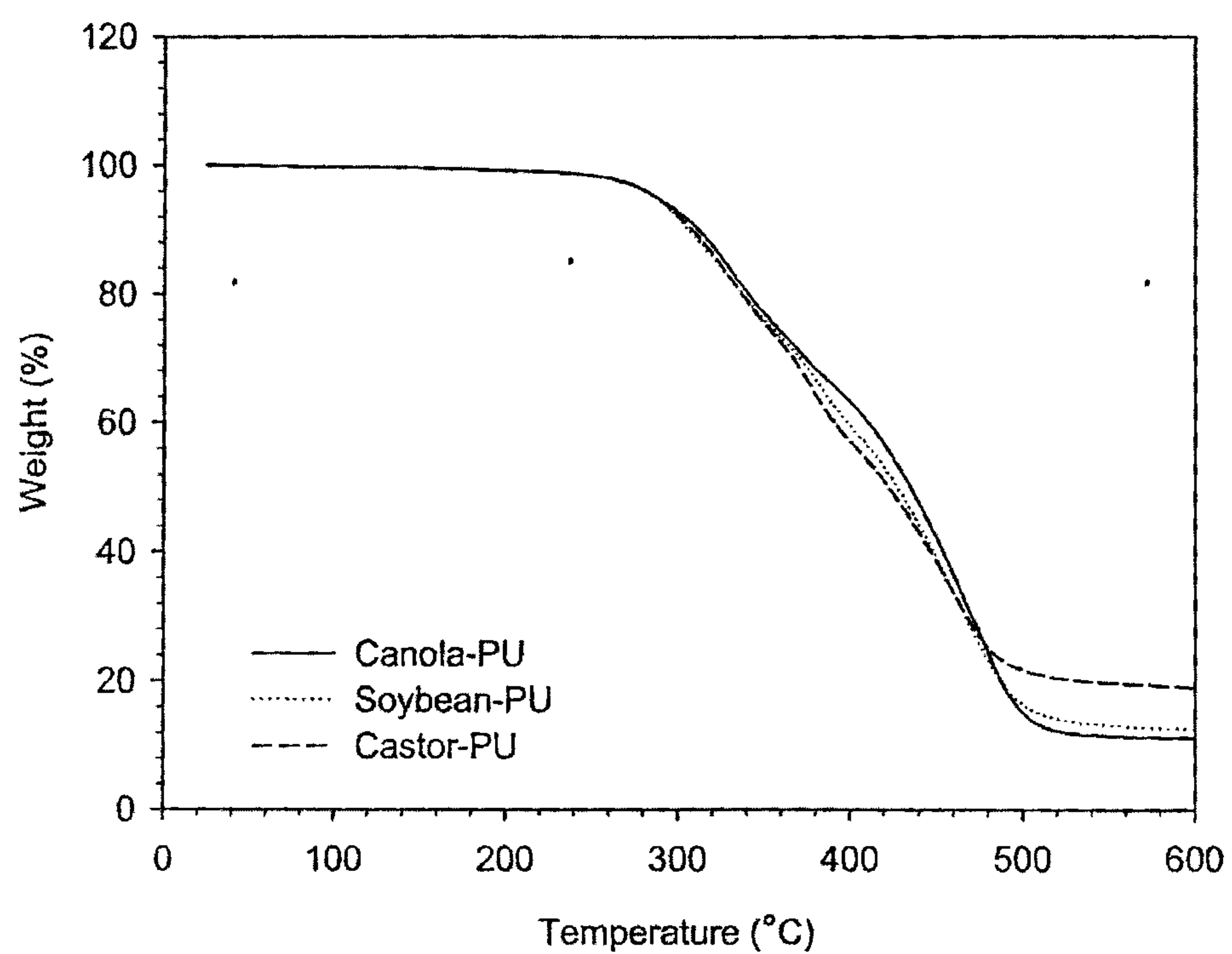


Figure 30(b): Derivative TGA curves polyurethane foams. (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

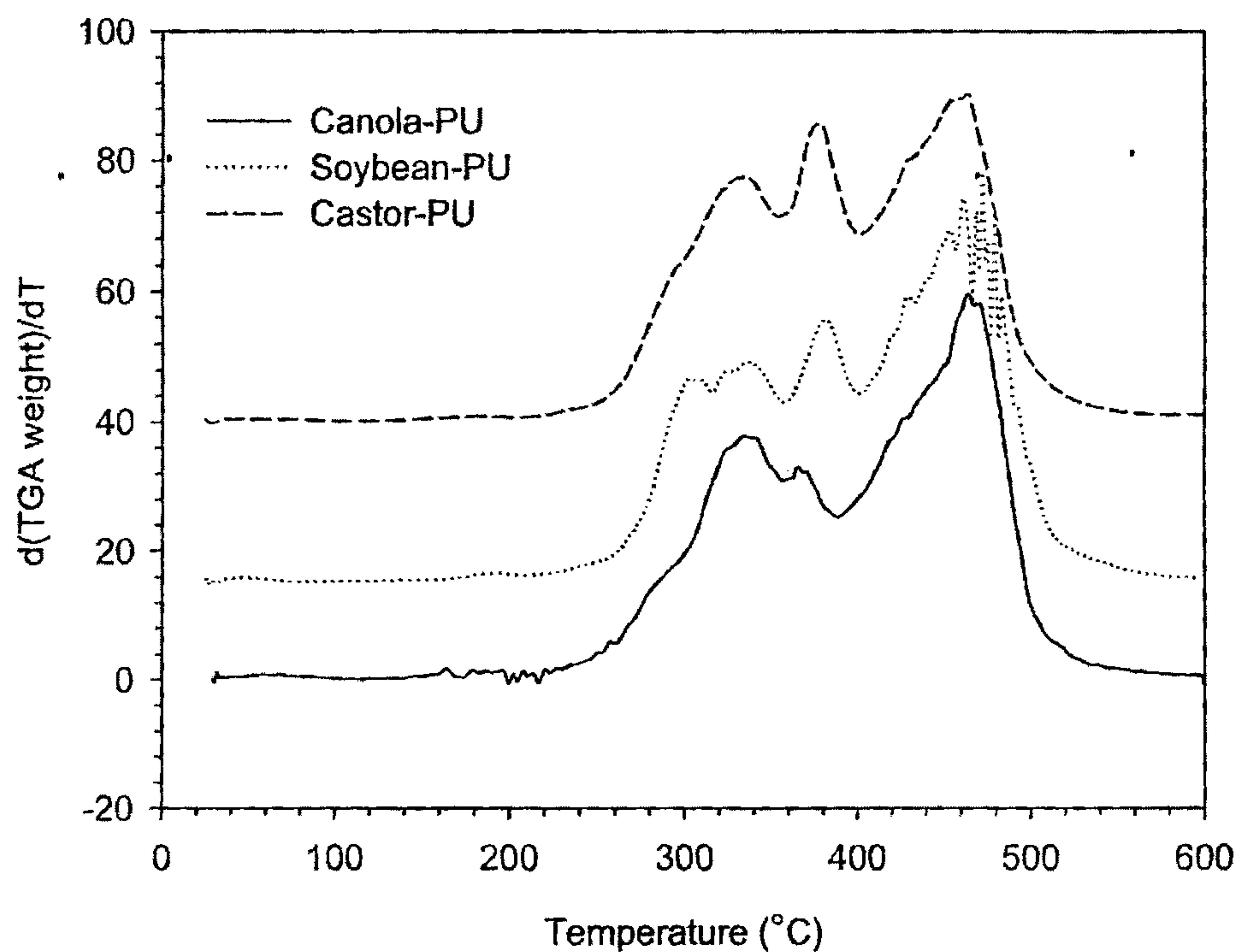


Figure 31: Compressive strength vs. strain of polyurethane foams. (—) Canola oil based polyurethane (Canola-PU), (·····) Soybean oil based polyurethane (Soybean-PU), and (---) Castor oil based polyurethane (Castor-PU).

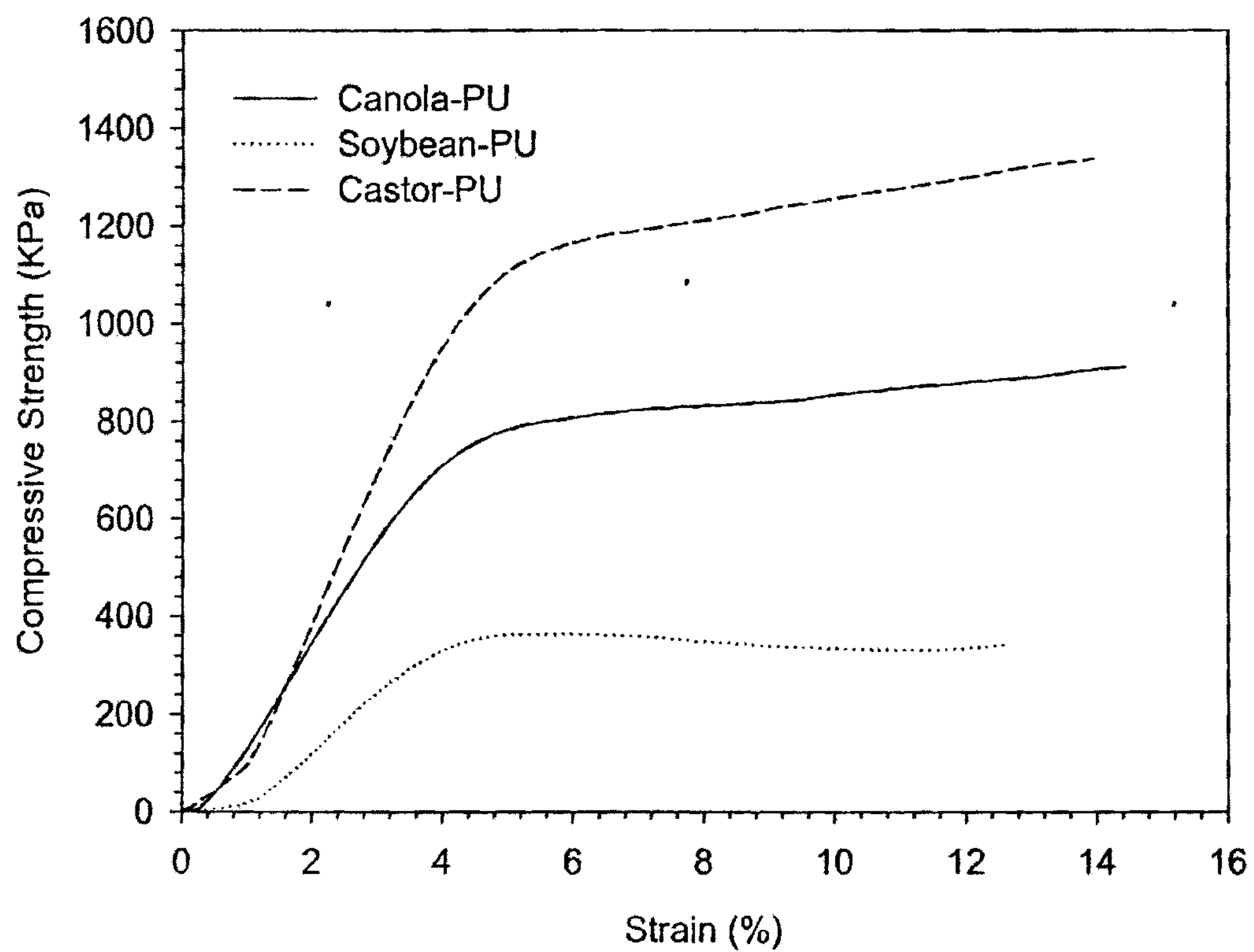


Figure 33: HPLC of Polyols Produced with Pd-C , Raney Ni System

- 1: Diol. Retention time: 15.03mins
2: Triol. Retention time: 25.48mins

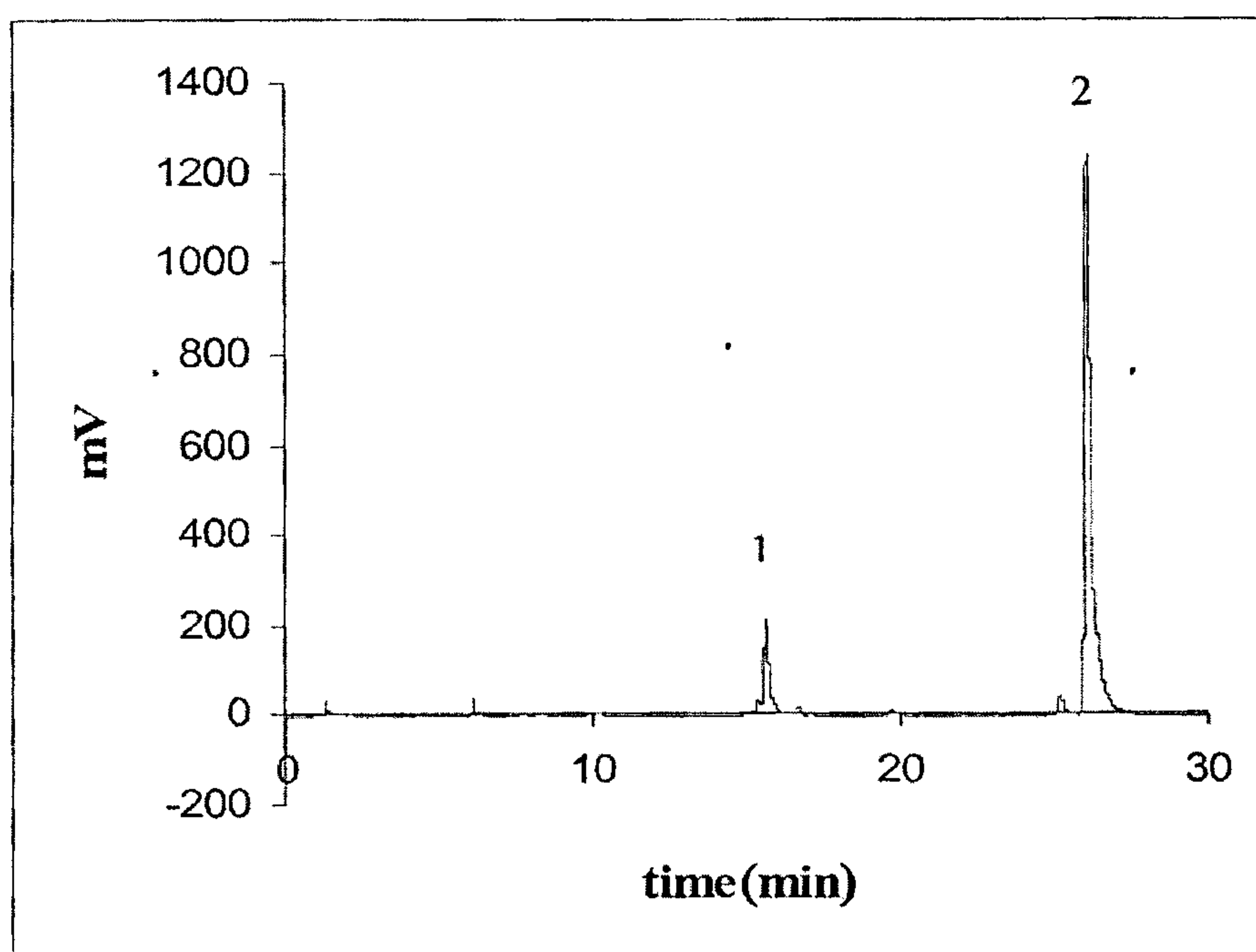


Figure 34: HPLC of Polyols Produced with Zinc, Raney Nickel System

- 1: Unreacted TAGs. Retention time: 5.53mins
2: Diol. Retention time: 15.03mins
3: Triol. Retention time: 25.48mins

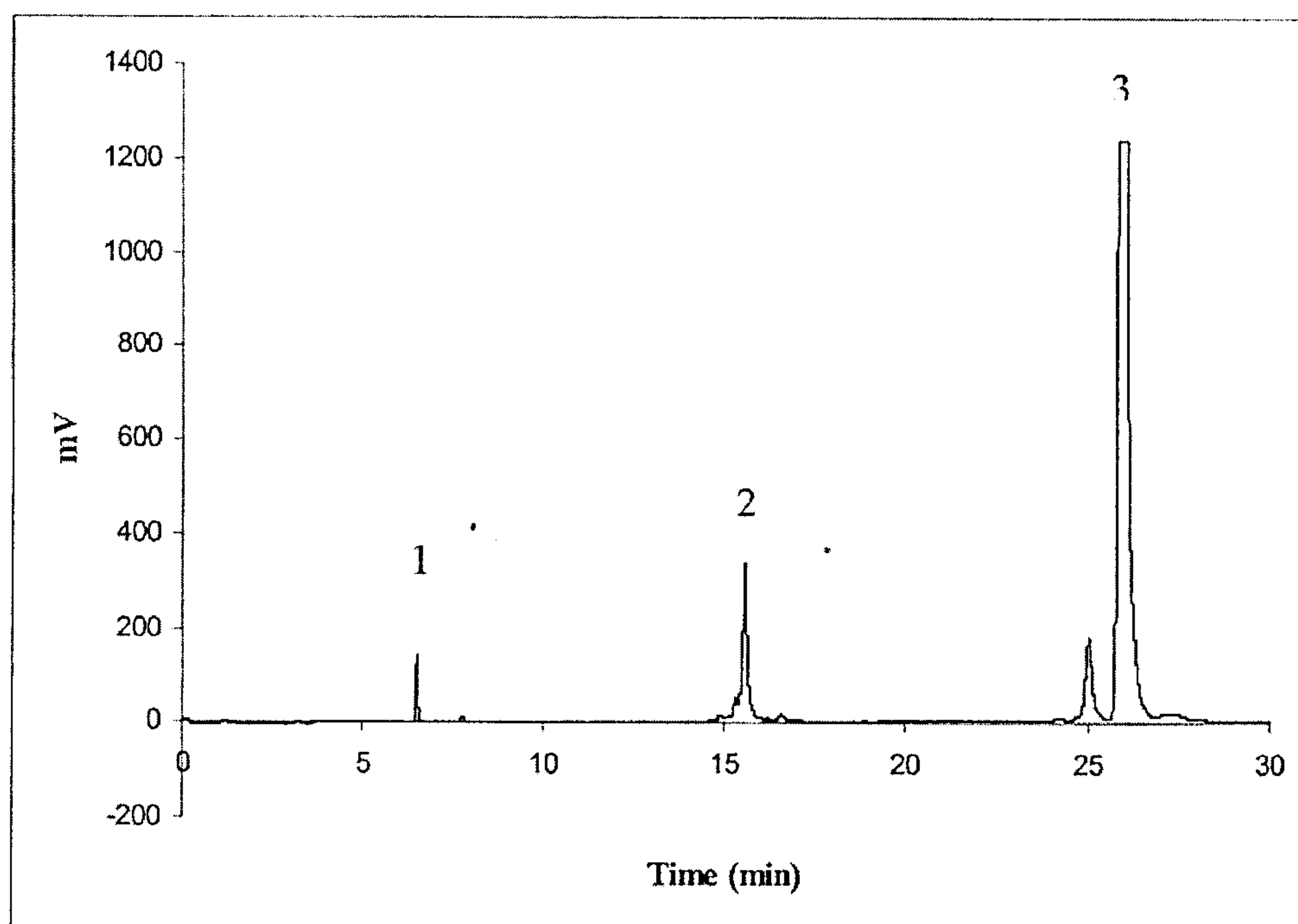


Figure 35: HPLC of Polyols Produced with Recycled Ethyl Acetate

1: Diol. Retention time: 15.03mins
2: Triol. Retention time: 25.48mins

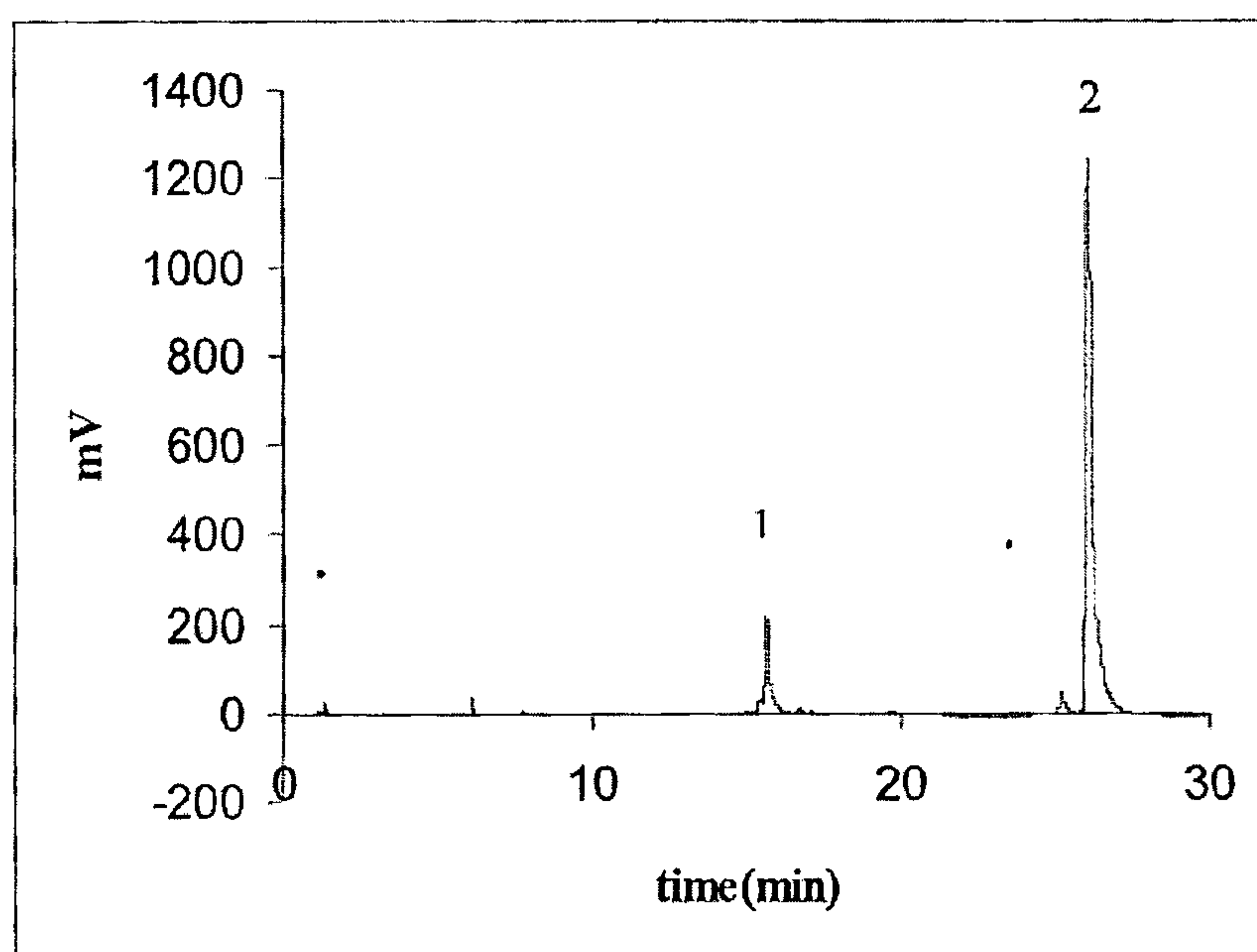


Figure 36(a): Viscosity as a function of time. of: (a) Ethyl Acetate Canola Oil Based Polyols, (b) Recycled Ethyl Acetate Canola Oil Based Polyols.

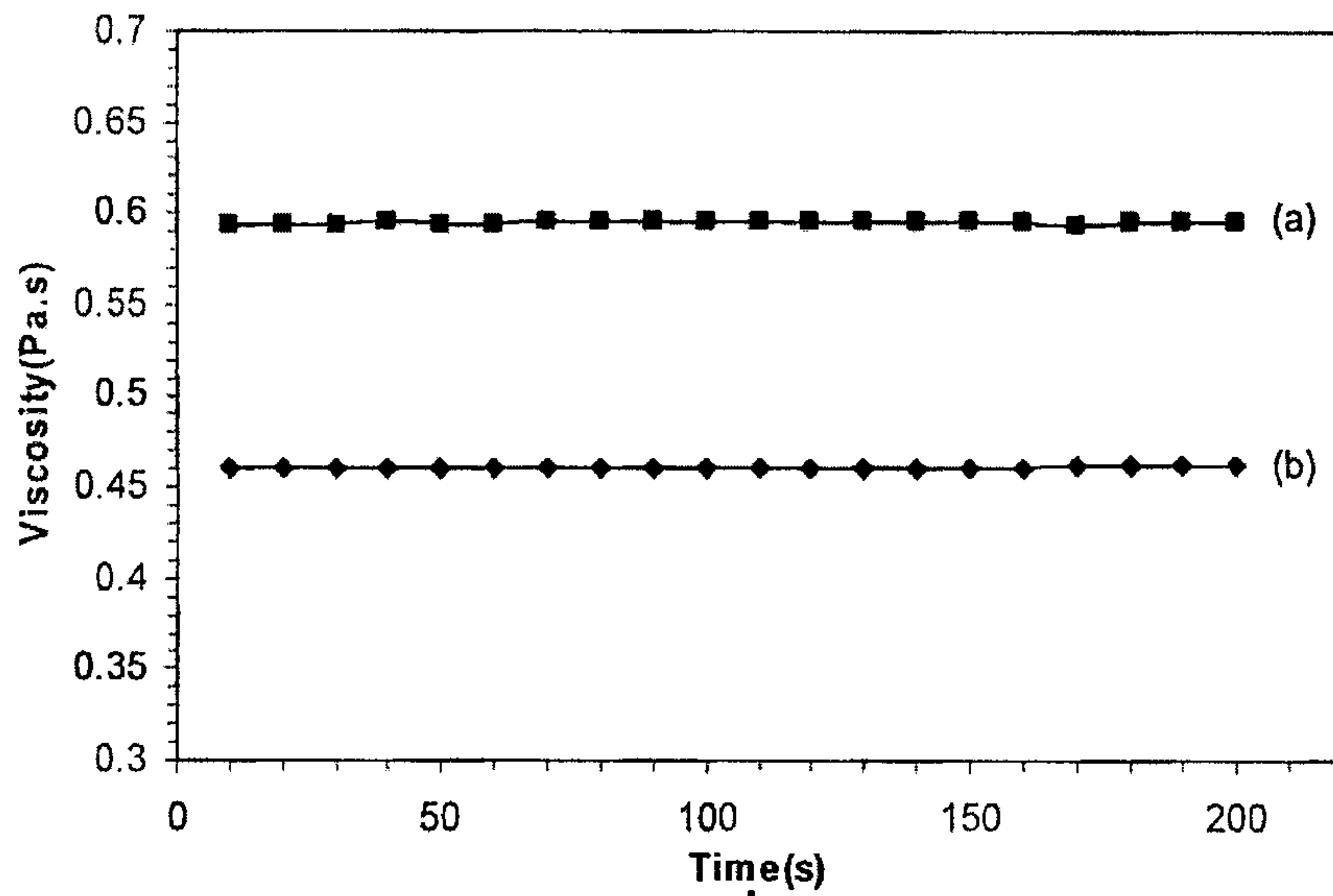


Figure 36(b): Viscosity as a function of temperature of: (a) Ethyl Acetate Canola Oil Based Polyols, (b) Recycled Ethyl Acetate Canola Oil Based Polyols..

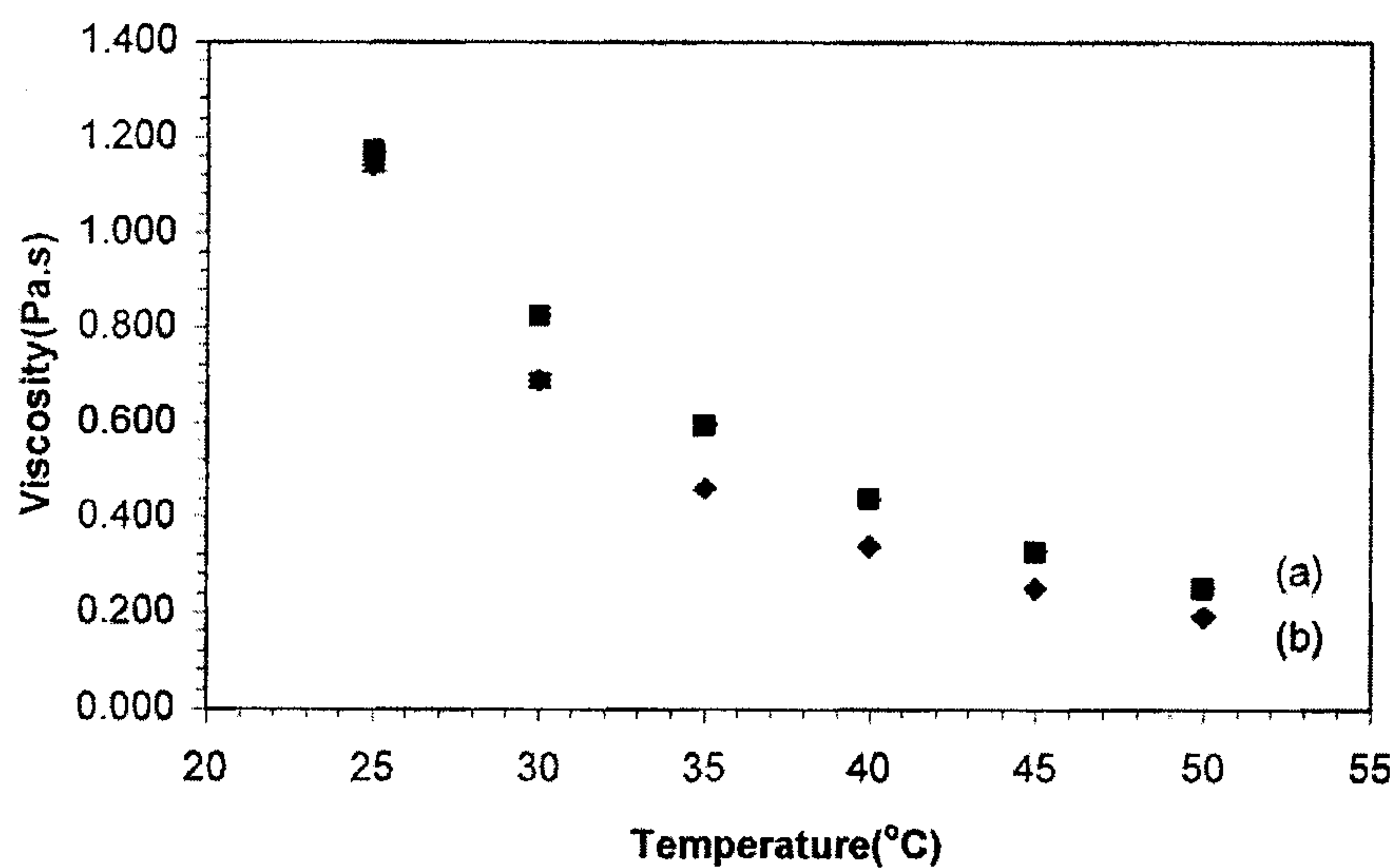


Figure 37(a): Storage moduli of polyurethane foams. (a) Ethyl Acetate Canola Oil Based PU (EACOBPU) and (b) Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU)

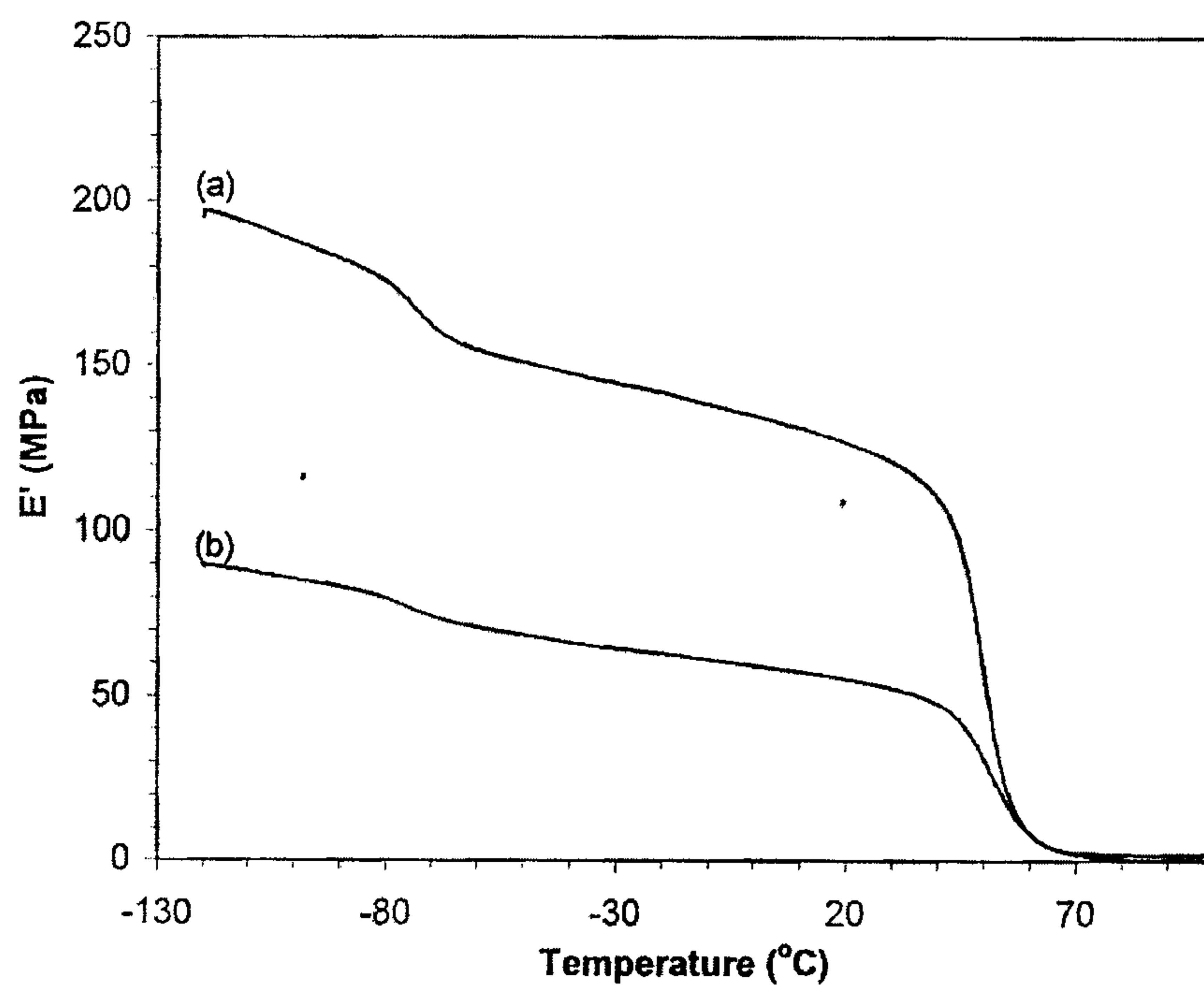


Figure 37(b): Loss moduli. (a) Ethyl Acetate Canola Oil Based PU (EACOBPU) and
(b) Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU)

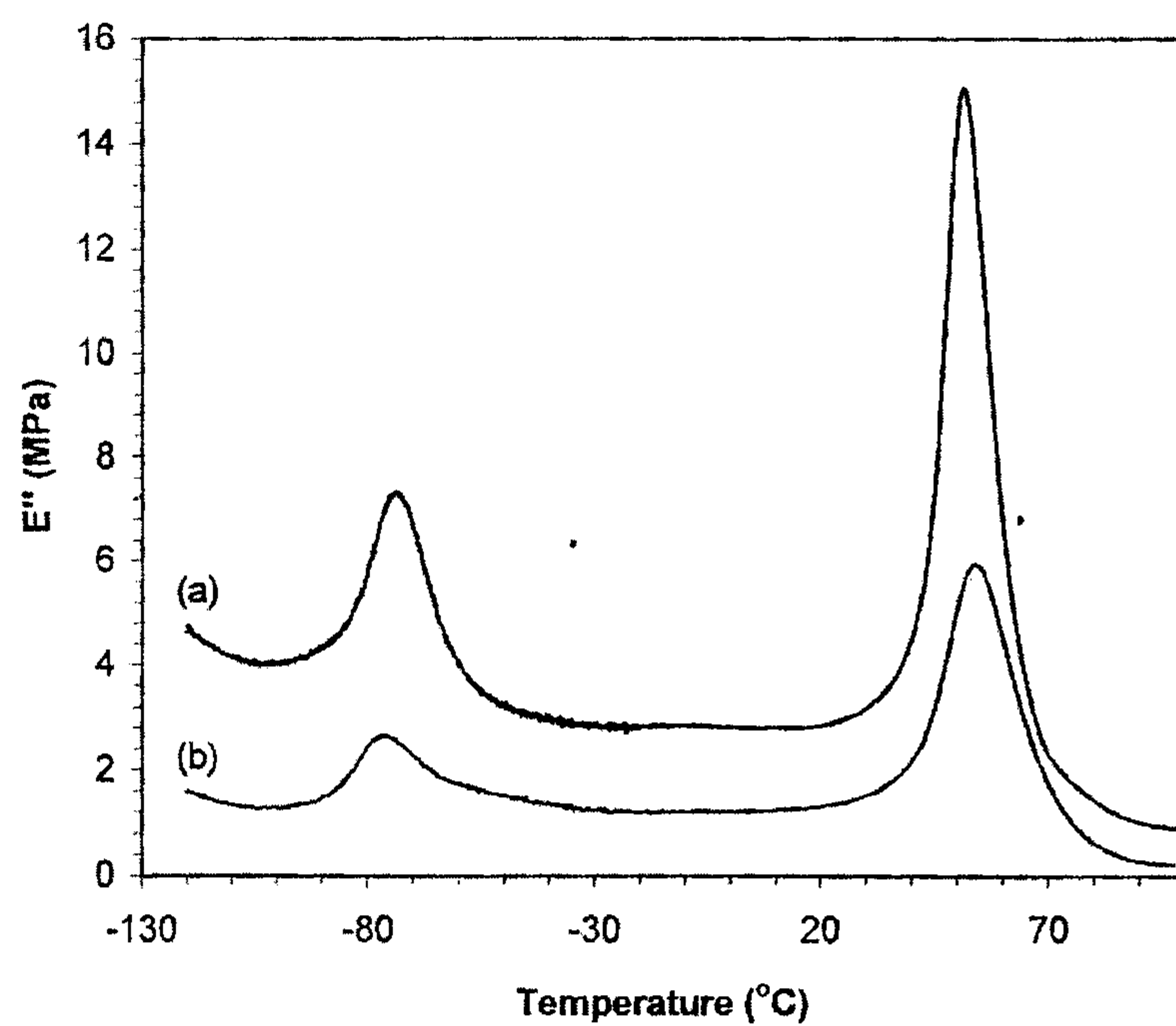


Figure 37(c): Tan δ of polyurethane foams. (a) Ethyl Acetate Canola Oil Based PU (EACOBPU) and (b) Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU)

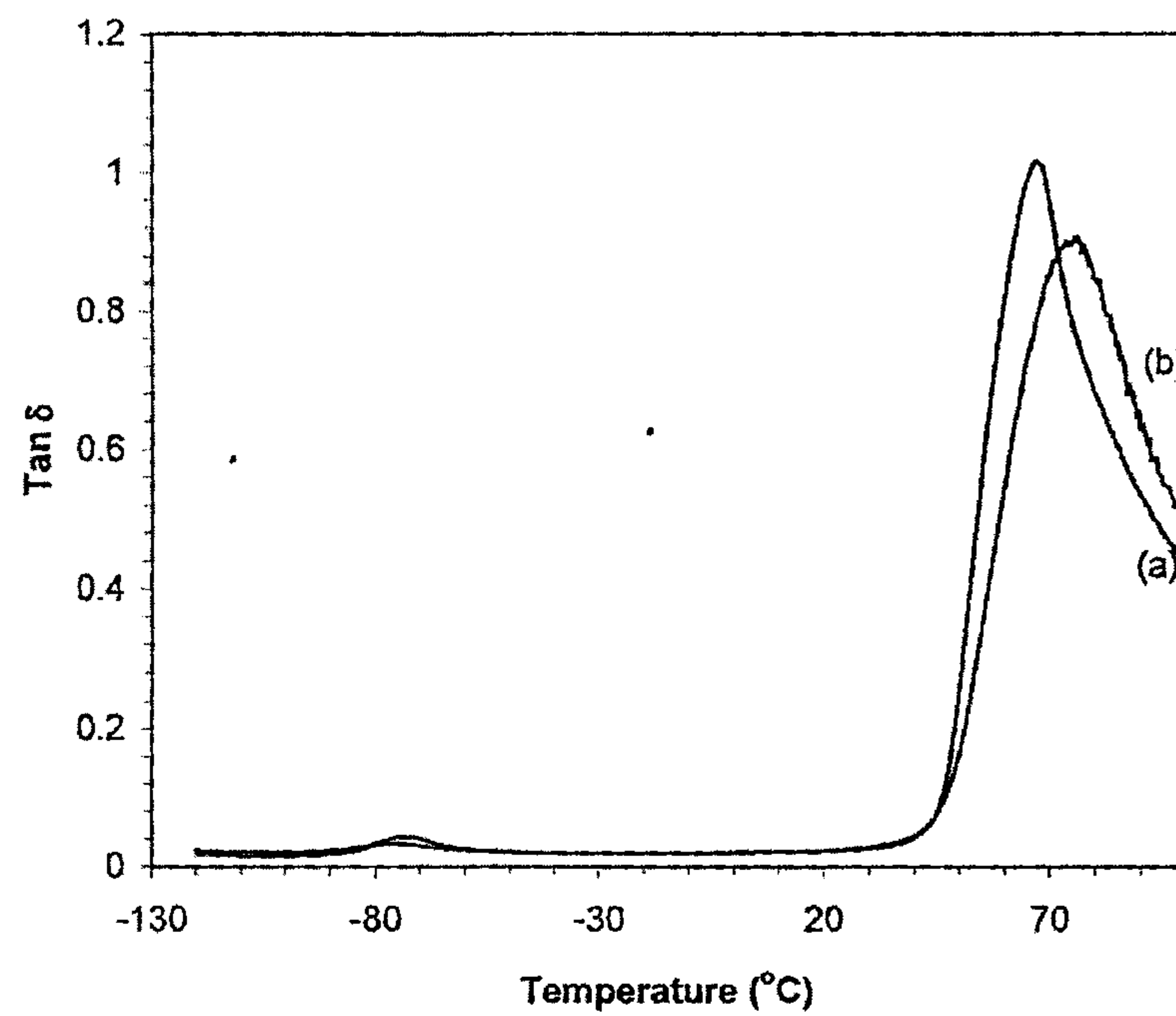
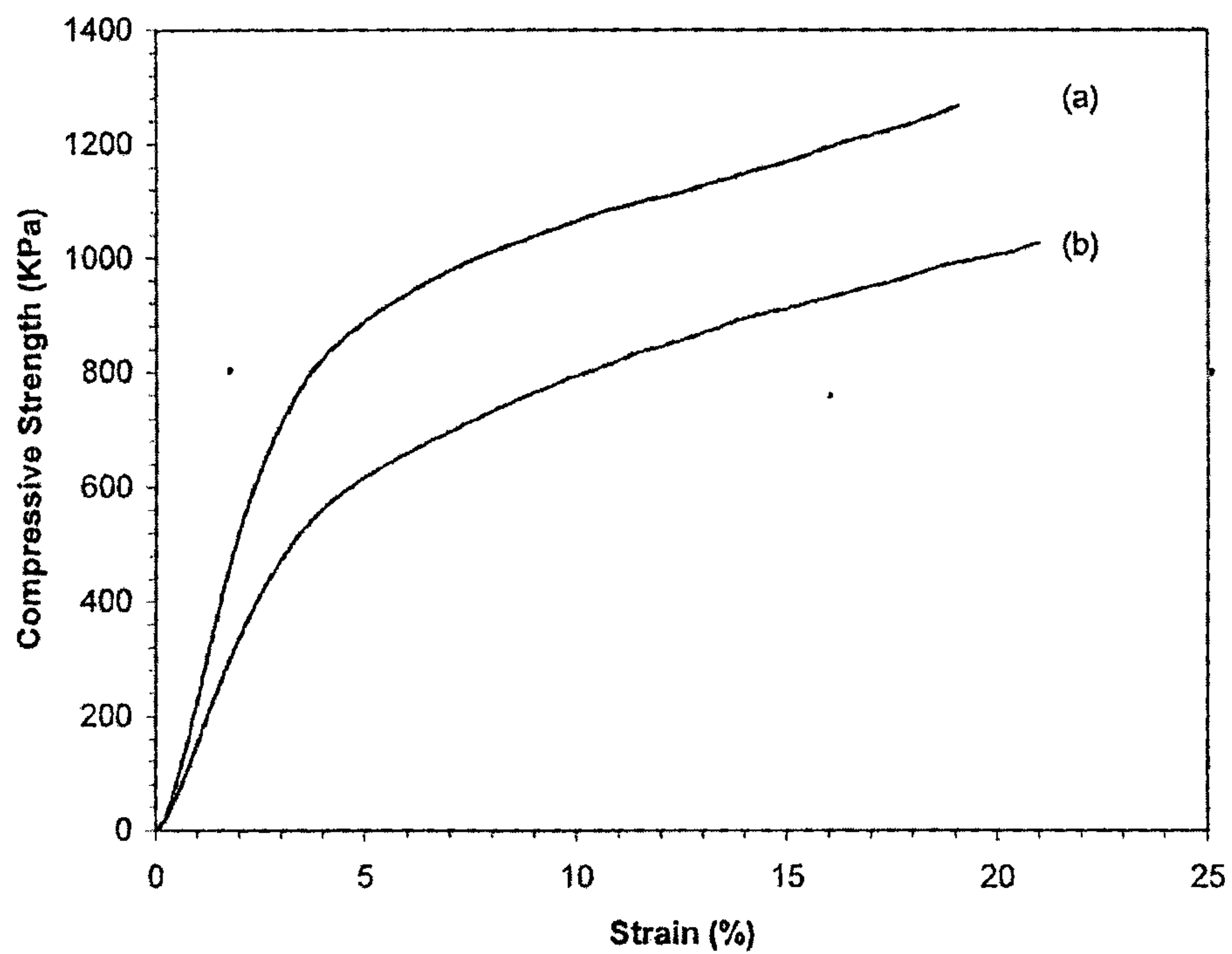


Figure 38: Compressive strength vs. strain of polyurethane foams. (a) Ethyl Acetate Canola Oil Based PU (EACOBPU) and (b) Recycled Ethyl Acetate Canola Oil Based PU (REACOBPU)



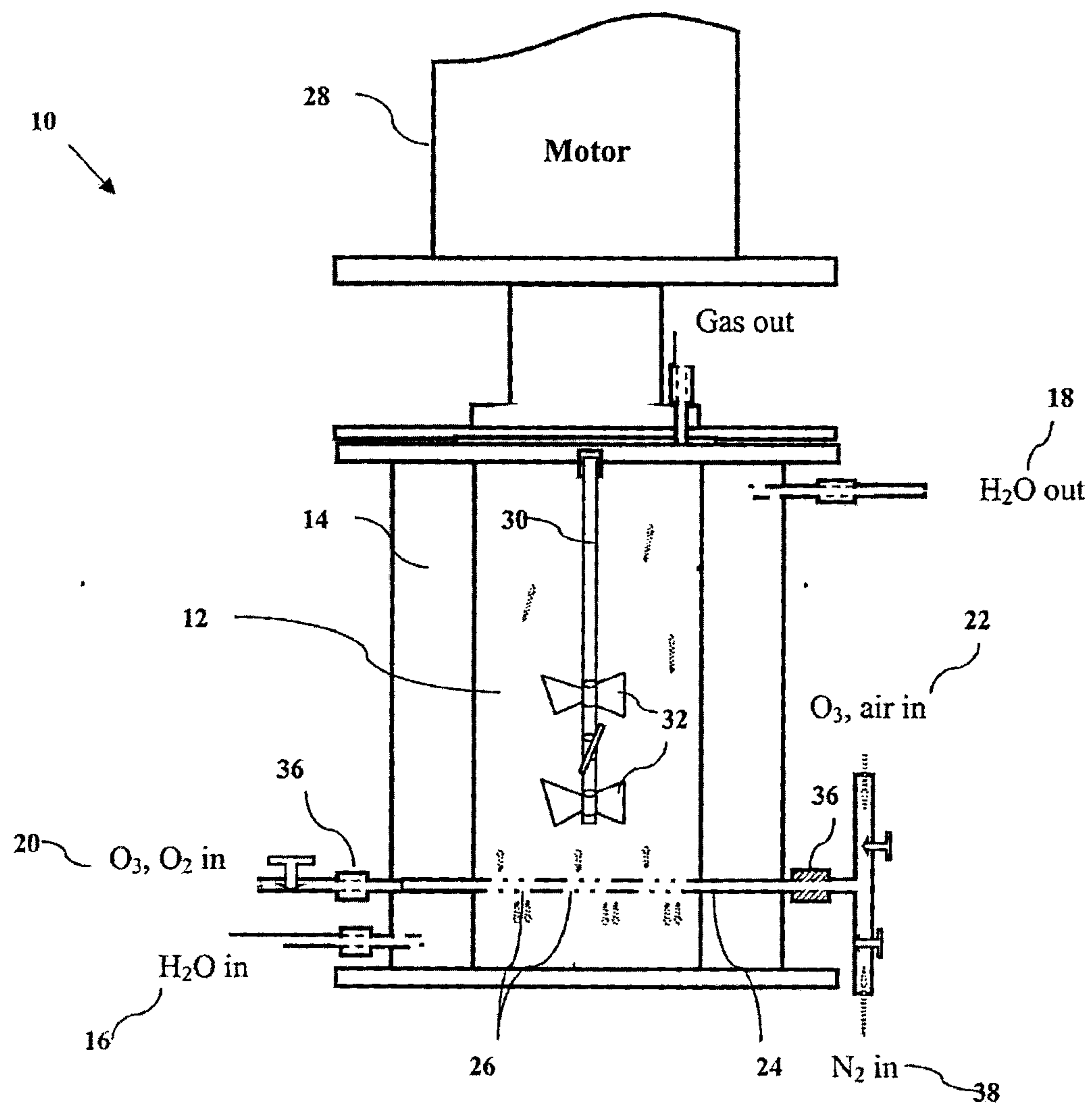


Figure 39

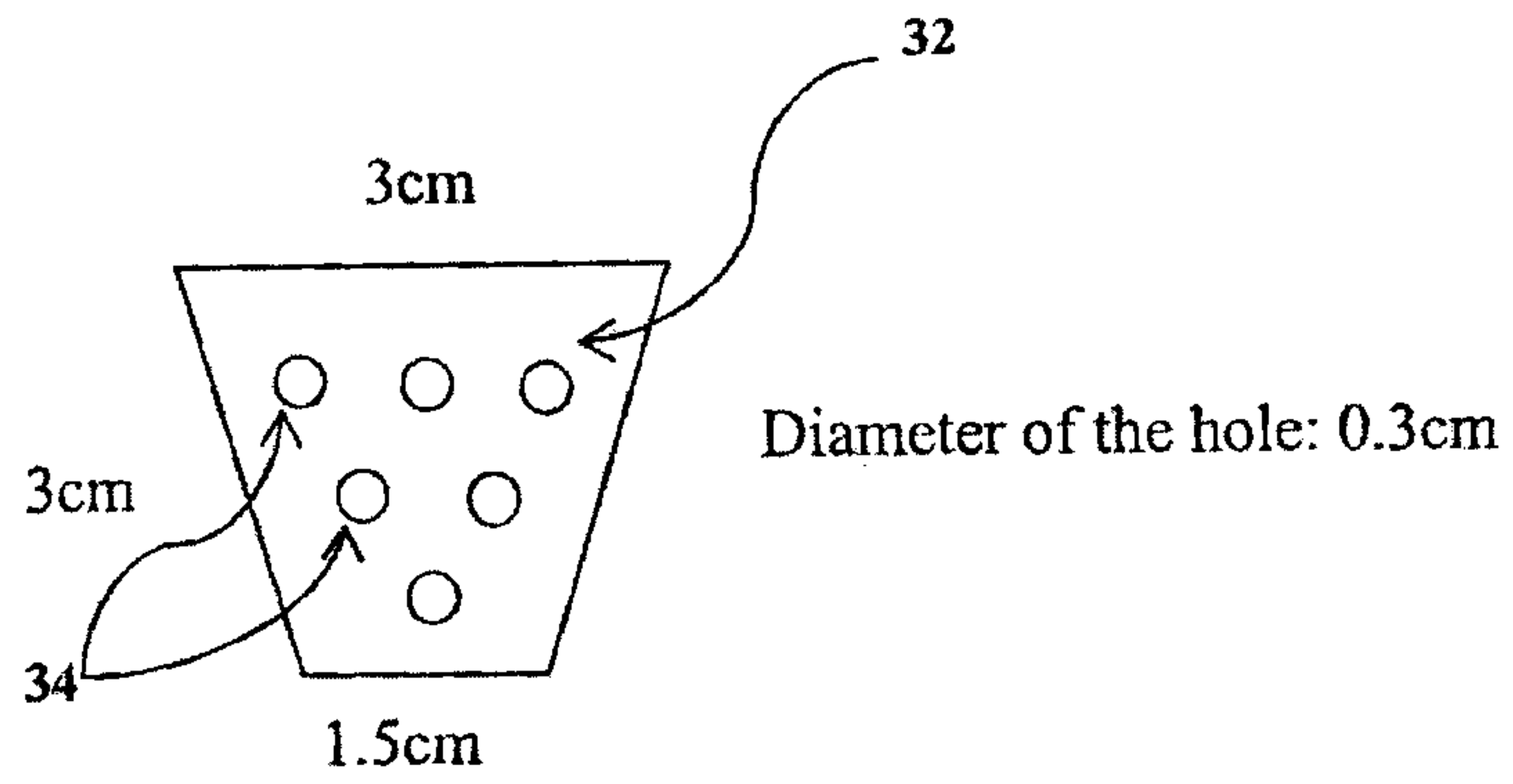


Figure 40(a)

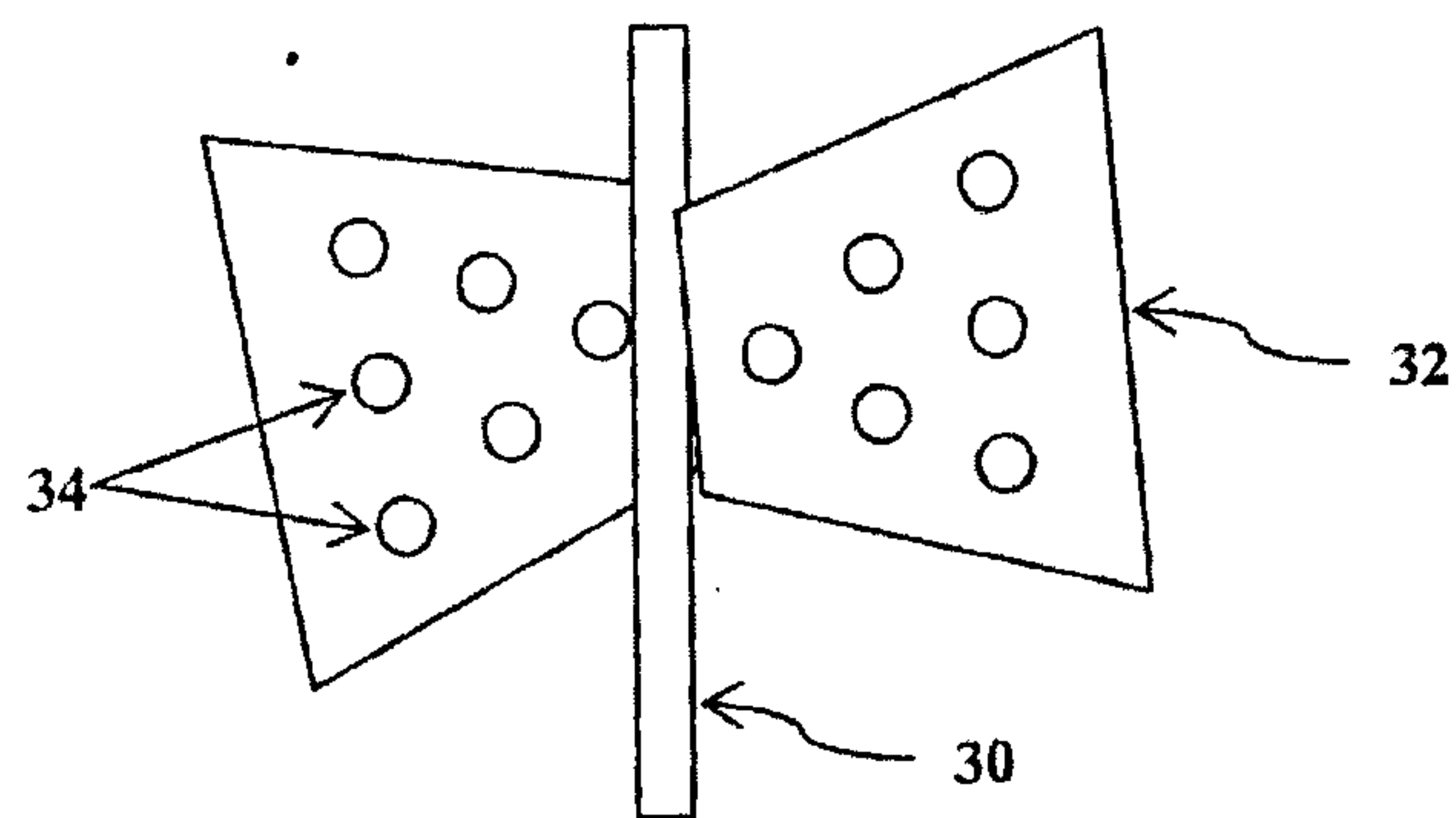


Figure 40(b)

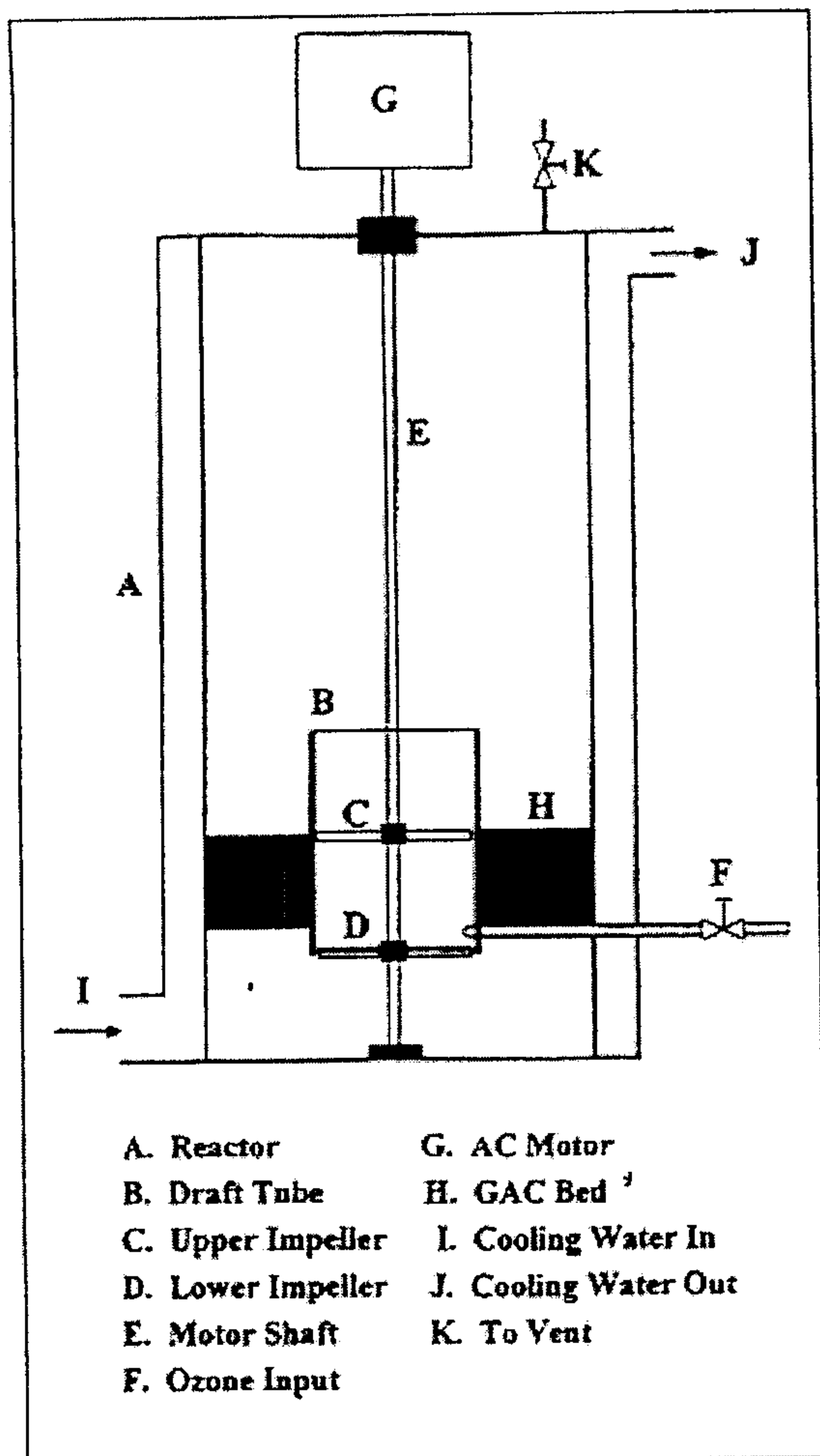


Figure 41 (Prior Art)

* Granular Activated Carbon Bed