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3,243,413

ELASTOMERIC POLYESTERS SYNTHESIZED
FROM COPOLYETHERS

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This invention relates to elastomeric polymers and more particularly to highly elastic polyester compositions suitable for the production of various products in which high elastic return is required. More specifically the invention relates to novel highly elastic polymeric compositions useful in the production of filaments, fibers, films and other shaped articles having superior elastic properties as well as high tenacity or tensile strength.

In recent years filaments, fibers, films and the like produced from various polyester compositions have become very important to the textile industry. However, in some cases it has been extremely difficult to attain in one and the same material the combination of properties desired such as the required melting point, tensile strength and, in elastic materials, a good elastic recovery. The difficulty of obtaining the desired combination of properties has been recognized by some of the leading researchers in the polymer field. For example, in part II of an article by W. Hale Charch and Joseph C. Shivers appearing in the Textile Research Journal for July 1959, 29, pages 536-540, entitled "Elastic Condensation Blocked Co-Polymers" these researchers state "For the synthetic fiber technologist it is significant that many elastic polymer structures possess no chemical cross links; hence they can be melted or dissolved and spun into fine fibers by conventional methods. Unfortunately, however, the melting points of typical fibers from the classes of polymers mentioned above are too low to permit them to be ironed when used along with other fibers in a fabric. Hence, if one would have an elastic textile fiber, one confronts the awkward problem of combining good elastic properties, which call for a low polymer melting point and low transition temperature, with a high ironing temperature, which calls for a high melting point, in one and the same polymer."

In an apparent attempt to deal with some of the problems referred to in the Charch and Shivers article and to produce an elastomeric filament or fiber material having the desired elastic and other physical properties there is described in British Patent 779,054 the production of a polyester material containing 35-75 percent by weight of poly(tetramethylene glycol) from a glycol such as ethylene glycol and aromatic dibasic acids or their esters. While apparently good elastic properties are attained in filaments or fibers produced from such compositions, such fibers are said to have a tensile strength of the order of 0.1 gram per denier, which experience has shown is insufficient to meet the demands of the textile trade for a polyester filament or fiber material suitable for use in the manufacture of elastic or stretchable fabrics such as those employed in foundation garments, self-supporting stockings and similar elastic fabric constructions.

In another article by T. B. Marshall entitled "Manmade Elastic Yarns" appearing in Textile Industries, 125, 8:75-80, August 1961, the author states: "For more than 13 years, chemists have been working actively on the development of elastomeric fibers that would represent an improvement over the natural and synthetic rubber yarns in common use. The first approaches were in the direction of modifying nylon and polyester polymers, but the fibers obtained, while highly promising, always turned out to be deficient in some respect, such as in hydrolytic

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instability or excessive stress decay. Garments that couldn't stand hot water or ones that grew appreciably larger during the course of a day's wearing would have had little attraction for the American woman."

The U.S. counterpart to British Patent 779,054, namely, U.S. patent to Shivers, 3,023,192, issued February 27, 1962, describes the preparation of segmented copoly(ether ester) elastomers by modification of polyesters melting above 200° C. with 35 percent to about 75 percent by weight of poly(ether ester) units derived from difunctional polyethers of molecular weight of 350 to 6,000. Such elastomeric compositions are described as having a high elongation, a low degree of stress decay, and satisfactory melting temperatures.

The elastomeric compositions of the instant invention are distinguished from those of the Shivers patent in a number of respects. Firstly, the amount of polyether used in the modification of the high melting polyester lies outside the limits described as useful in the above-mentioned Shivers U.S. Patent 3,023,192. It is surprising that the elastomeric compositions of the present invention have useful elastomeric properties in view of the teachings of the above-mentioned article by Charch and Shivers since in this article these researchers point out that above a certain limit of modification elastomeric properties cease to exist and the composition so obtained is a gum that is, a resinous mass of no fiber-forming value. Secondly, the elastomeric compositions of the instant invention show considerably improved elastomeric properties in the temperature range from room temperature down to 0° C. In this temperature range polyester elastomers frequently show a high degree of set after they have been elongated for an extended period of time. The term "set" is herein used to describe that condition where a sample of an elastomer after elongation does not return completely to its original dimensions. The compositions of the instant invention, on the other hand, as will be more fully set forth hereinafter, display a greatly reduced degree of set in this low temperature range. Such a property is of great advantage, for example, in garments which are exposed to cold weather conditions. The Shivers U.S. Patent 3,023,192, describes the use of aliphatic glycols in conjunction with aromatic dicarboxylic acids to obtain the high melting polyester segment necessary for polyester compositions having satisfactory melting points. The aliphatic glycols described are entirely polymethylene glycols or branched chain derivatives thereof. There is no mention whatever of the cycloaliphatic glycols which have been found to be most useful in the instant invention. Of particular interest in the present invention is the cycloaliphatic glycol 1,4-cyclohexanedimethanol.

The present invention is an improvement upon or extension of the inventive concept of the polyester compositions described in our prior U.S. Patent 2,901,466, issued August 25, 1959, entitled "Linear Polyester and Polyester Amides From 1,4-Cyclohexanedimethanol." This application is also closely related to our copending application Serial No. 145,433, filed October 16, 1961, now abandoned and superseded by continuation-in-part Serial No. 215,768, filed on August 9, 1962.

The invention has for its principal object to provide a highly elastic polyester composition especially adapted to the manufacture of filaments, fibers, yarns, films and other shaped objects having excellent elastic properties.

Another object is to provide a highly elastic polyester composition from which filaments, fibers and yarns having satisfactory tenacity, high elongation, good modulus of elasticity, excellent elastic return, high ironing temperature and excellent hydrolytic stability may be produced.

A further object is to provide a highly elastic polyester composition from which filaments, fibers and yarns having the above mentioned physical properties may be obtained and also characterized by the fact that they have a substantially reduced tendency to develop set after extended periods of elongation and particularly show a reduced tendency to develop this set at low temperatures.

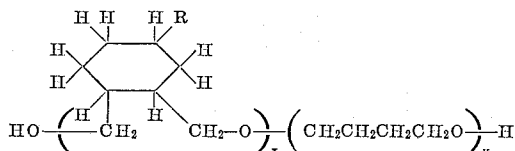
Another object is to provide stable filaments, fibers, and yarns having satisfactory tenacity, high elongation, good modulus of elasticity, excellent elastic return, high ironing temperature and excellent hydrolytic stability.

Another object is to provide filaments, fibers, yarns, films and other shaped objects having the above mentioned desired physical properties and also characterized by the fact that they have a substantially reduced tendency to develop set after extended periods of elongation at temperatures ranging from room temperature to 0° C.

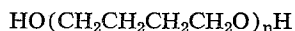
Another object is to provide stable films and other shaped objects having satisfactory tenacity, high elongation, good modulus of elasticity, excellent elastic return and excellent hydrolytic stability having a substantially reduced tendency to develop set after extended periods of elongation and particularly at low temperatures.

Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in one embodiment, comprises forming a highly elastic, highly polymeric polyester by reacting (A) at least one compound selected from the class consisting of the dibasic carboxylic acids and their esters and (B) at least one member of the group consisting of the cis- and trans- isomers of 1,4-cyclohexanedimethanol and either (C) the copolyether glycol having the structural formula:



wherein R is a substituent selected from the group consisting of hydrogen or methyl, x and y are integers greater than zero and selected from the group defined by the equations x is less than y and $x+y=14$ to 130 and wherein the two repeat units are distributed in a random manner in the copolyether molecule, or (D) a mixture of the copolyether glycol described hereinabove and the ether glycol having the structural formula:



wherein n is an integer from 14 to 80, the compound being commonly known as poly(tetramethylene glycol).

It is well known in the art that for a polymer to have elastic properties it must consist of alternate so-called "hard" and "soft" segments. The hard segment has a rigid structure and serves as an anchor point to prevent the polymer molecules from slipping over one another. This segment may be an actual chemical link between adjacent polymer chains or it may be a rigid high melting crystalline unit such as a short block of a high melting polyester, polyamide, polyurea or the like. The soft segment must be a long flexible molecule capable of assuming a compact, coiled configuration when not under stress. Under stress it must extend freely to a relatively linear configuration but return to the coiled structure when the stress is removed. Thus it should be free of any intermolecular forces stronger than the retractive forces which tend to return the molecule to the coiled conformation. Such a situation may arise when the soft segments crystallize while the molecules are held in an extended configuration. If the degree of crystallinity is high enough, the retractive forces are overcome and the molecule is held in the extended position. Fibers of such a material would have unsatisfactory elastic properties because they would show a high degree of set.

The commonly used soft segments are low melting polyesters or polyethers derived from polyether glycols. Of this latter class the most useful is poly(tetramethylene glycol):



wherein n is an integer from 14-70.

Useful elastomeric polyesters have been prepared employing this polyether glycol as the source of the soft segments. However, the melting point of poly(tetramethylene glycol) is approximately 35-40° C. In polyesters and the like prepared from this compound the soft segment will, therefore, tend to crystallize at some temperature near the melting point of the polyether glycol. In practice, it has been found that this soft segment does partially crystallize at 20-25° C. particularly when a fiber, film or other object made from such a polymer is held in a stretched condition below this critical temperature. This partial crystallization prevents the complete return of the stretched object to its original dimensions and thus impairs its usefulness. The temperature at which this loss of elastic properties occurs is in the range of the temperatures at which fibers and films are usually used, i.e., from near normal room temperature to about 0° C. For this reason, a lower-melting polyether glycol which retained the desirable qualities of poly(tetramethylene glycol) would be of considerable utility for the preparation of elastomeric polyesters and the like. That the soft segment remain liquid at relatively low temperatures is a necessary but not sufficient requirement for the production of a good elastomer therefrom. For example, polypropylene glycol has a satisfactorily low melting point but, because of other defects, does not give good elastomeric polyesters. Also, the homopolymer of 8-oxabicyclo[4:3:0]nonane, while a liquid even at 0°, gives polyesters which have little or no elasticity. Thus, it cannot be known without experiment whether a particular non-crystallizing liquid polyether glycol will be useful for preparing elastomeric polyesters and the like. In fact, of a large number of such liquid polyether glycols that have been tested only those described herein, namely, the copolymer of tetrahydrofuran and 8-oxabicyclo[4:3:0]nonane or 3-methyl-8-oxabicyclo[4:3:0]nonane have proven completely satisfactory for the preparation of useful polyester elastomers of the type herein described.

The copolyether glycols which are the copolymers of tetrahydrofuran and 8-oxabicyclo[4:3:0]nonane or 3-methyl-8-oxabicyclo[4:3:0]nonane and which have proven valuable in the practice of the present invention are the invention of Gerald R. Lappin and described and claimed in his copending application Serial No. 231,588, entitled Copolymeric Ether Glycol filed on the same date as this application, viz., October 18, 1962.

As indicated above, we have found that mixtures of poly(tetramethylene glycol) and the copolymerization product of tetrahydrofuran with 8-oxabicyclo[4:3:0]nonane or with 3-methyl-8-oxabicyclo[4:3:0]nonane may be employed. It is a generally recognized principle of organic chemistry that the addition of small quantities of a compound to a second compound will depress the melting point of the second compound. Thus it can be seen that adding quantities of the copolyether glycol to poly(tetramethylene glycol) will depress the melting point of the latter compound. Such mixtures of these two polymeric ether glycols will remain liquid at room temperature, if the correct ratio of the two polyethers is chosen. Elastomeric polyesters prepared from such mixtures will then have soft segments which will not have a tendency to crystallize during extended periods of elongation. In other words, using a mixture of poly(tetramethylene glycol) and the copolyether prepared from tetrahydrofuran and 8-oxabicyclo[4:3:0]nonane or 3-methyl-8-oxabicyclo[4:3:0]nonane gives elastomeric polyesters which have elastic properties equal to those compositions prepared from the copolyether glycol alone.

In accordance with our invention it has been found that the poly(tetramethylene glycol) and the copolyether glycol should preferably be mixed in such proportions that the mixture contains on the average at least 5 mole percent of the modifying agent 8-oxabicyclo[4:3:0]nonane or 3-methyl-8-oxabicyclo[4:3:0]nonane. For example, one part by weight of a copolyether glycol prepared from a mixture consisting of 80 mole percent tetrahydrofuran and 20 mole percent 8-oxabicyclo[4:3:0]nonane can be mixed with a maximum of three parts of poly(tetramethylene glycol) so that the average content of the mixture is 5 mole percent of 8-oxabicyclo[4:3:0]nonane. Polyesters prepared from such mixtures possess good low temperature elastomeric properties.

In accordance with the invention the reaction to produce the elastomeric polyesters described herein is carried out in such a manner that the dihydroxy moiety [cyclohexanedimethanol plus the poly(tetramethylene glycol)] contains at least 50 mole percent of (B). The polyether consequently will constitute less than 50 mole percent of the dihydroxy moiety. To obtain the properties outlined in the objects of this invention as hereinabove stated the polyether component should be present in an amount corresponding to 50-93 weight percent of the final polyester. Polyesters of this invention have a crystalline melting point greater than 150° C. and an inherent viscosity of at least 1.0 and preferably above 1.4 and desirably within the range of 1.4-4.0.

The copolyether glycol represented by the structural formula set forth above may be considered as a mixture of low and high molecular weight compounds. It is preferred, however, that the glycol be a mixture of polymers which will have a relatively narrow range of molecular weight. Thus the sum of x and y of the formula represents the average total number of repeat units present in the copolyether molecule. For the production of polyester products of optimum elastomeric properties according to our invention as, for example, filaments and fibers, we have found that x plus y preferably has an average value of 30 to 70 which represents average molecular weights in the range of 2200 to 5000.

In those cases in which mixtures of the copolyether glycol and poly(tetramethylene glycol) are used to prepare the elastomeric compositions of our invention, the preferred average molecular weight of the mixture lies within the range 2200 to 5000. Since, as stated hereinabove, it is preferable to have a narrow range of molecular weights, it is therefore preferable that the components of the mixture have approximately the same molecular weights. However valuable compositions are also obtained using mixtures prepared from components of different molecular weights within the range of 1,000 to 6,000.

Elastomeric compositions having valuable properties can be prepared containing 50 to 93 weight percent of the mixed polyether glycols. The preferred compositions contain 75 to 87 weight percent of these mixed ether glycols.

The dicarboxylic acids which are useful for the preparation of the elastomeric polyesters of the instant invention are those in which the carboxylic acid groups are attached to a hexacarbocyclic nucleus in para relationship and the entire hydrocarbon moiety contains 6 to 20 carbon atoms. Examples of hexacarbocyclic dicarboxylic acids wherein the carboxy radicals are attached to a hexacarbocyclic nucleus in para relationship include terephthalic acid, trans-1,4-cyclohexanedicarboxylic acid, 4,4'-benzophenonedicarboxylic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-methylenedibenzoic acid, 1,2-di(carboxyphenoxy)ethane, 4,4'-dicarboxydiphenyl ether, etc. All of these acids contain at least one hexacarbocyclic nucleus. Fused rings can also be present such as in 1,4 or 1,5 or 2,6 or 2,7-naphthalenedicarboxylic acid. The hexacarbocyclic dicarboxylic acids are preferably those containing a trans-cyclohexane nucleus or an aromatic nucleus containing from one to two benzene rings of which at least one has

the usual benzenoid unsaturation. Of course, either fused or attached rings can be present. All of the compounds named come within the scope of this preferred group.

DEFINITIONS

For purposes of clarity and of properly disclosing and defining our invention, the following definitions are given:

Inherent viscosity (I.V.).—This property, represented by (η) , which is used as a measure of the degree of polymerization of a polymeric compound, is calculated from the equation:

$$(\eta) = \frac{\ln \eta_r}{C}$$

wherein η_r is the ratio of the viscosity at 25° C. of a dilute (approximately .25 percent by weight) solution of the polymer in a solvent composed of 60 percent by weight of phenol and 40 percent by weight of tetrachloroethane to the viscosity of the solvent itself, and C is the concentration of the polymer in grams per 100 cubic centimeters of the solution.

Tenacity or tensile strength.—This is a measure of the strength of the fiber, filament or yarn under study. It is expressed in grams per denier (g./d.) and is calculated by dividing the initial denier of the fiber under study into the tension (in grams) required to break the yarn. The values of tenacity reported in this invention were in each instance determined on a 2-inch specimen in an Instron tester manufactured by Instron Engineering Corporation, 2500 Washington Street, Canton, Massachusetts at a rate of extension of the specimen of 1000 percent per minute.

Elongation.—This is a measure of the extent to which a fiber, filament or yarn is stretched when it breaks. It is expressed as a percentage and is calculated by dividing the original length of the sample into the increase in length and multiplying by 100. Specifically, two marks 20 cm. apart are placed on the fiber or film sample and the sample is extended by hand until it breaks. The distance which separates the marks at the time of breakage is noted and the elongation calculated. The average of five or six such determination is used as the value of the elongation of the sample is question. Approximately eight seconds are required to pull the fiber sample to the breaking point and this represents a rate of elongation of approximately 3000 percent per minute.

Elastic recovery.—This property is a measure of the ability of a fiber, yarn, filament or film to return to its original length after elongation. For the purposes of this invention, the elastic recovery of a sample is determined by drawing the sample to an elongation of 400 percent and then allowing it to return to a relaxed state (but not "snap" back). The amount of elongation which is recovered divided by the original elongation and the result multiplied by 100 gives the percent elastic recovery.

Modulus of elasticity.—As used herein modulus of elasticity may be defined as the tension in grams per initial denier per percentage elongation necessary to stretch the sample to the stated percentage elongation. When measuring the modulus of films the tension may be expressed in pounds per square inch.

Critical set temperature.—In order to measure the permanent set of a fiber or film at various temperatures, the following test may be employed: A film, 5-6 mil in thickness is formed from polyester material and strips approximately 1/8 inch wide are cut therefrom. The strips are folded once and the open ends clamped so that a loop 30 mm. in length is formed. This loop is drawn to a length of 120 mm. (300 percent extension) and then allowed to contract to a length of 75 mm. (150 percent extension). The sample is held at this length for 16 hours at room temperature (24° C.) by means of a hook inserted through the closed end of the loop. In order to measure the degree of set of the sample at various temperatures the entire sample is immersed in a water bath cooled to about 0° C. (an ice-water-salt bath can be used

for lower temperatures). When the sample reaches temperature equilibrium it is released from the restraining hook and permitted to contract. The length is then measured and the percentage set calculated by dividing the increase in length by the original length of the sample (30 mm.) and multiplying by 100. The bath temperature is then increased by stirring in warm water. When the desired temperature is reached, the loop length is again measured. The temperature is again raised, and the length redetermined and so on. Temperature ranges of 0 to 30° C. are usually covered in 5° C. steps and the percentage set is plotted against temperature. The temperature at which the film strip has a length of 40 mm. (33⅓ percent set) is determined and this temperature, which is defined as the critical set temperature, is the numerical value used in any comparison. This same test may be performed using fibers in place of film strips.

Crystalline melting point.—This is defined as the temperature at which a sample of the polymer under test will flow under slight pressure on a Fisher-Johns melting point apparatus manufactured and sold by Fisher Scientific Company, 633 Greenwich St., New York 14, N.Y.

In the following examples and description we have set forth several of the preferred embodiments of our invention but they are included merely for purposes of illustration and not as a limitation thereof.

Example 1

A 250 ml. flask equipped with stirrer, nitrogen inlet and distillation head was charged with 8.56 g. (0.0308 mole) of dibutyl terephthalate, 7.5 g. (0.0520 mole) of trans-1,4-cyclohexanedimethanol, 33.0 g. (0.1 mole) of a polyether of number average molecular weight 3300 prepared from a mixture of 85 mole percent tetrahydrofuran and 15 mole percent 8-oxabicyclo[4:3:0]nonane, 12 g. of a chlorinated polyphenyl sold by Dow Chemical Company under the trademark Aroclor 5442, 0.4 g. of dilauryl thiodipropionate and 0.6 ml. of a 21 percent solution of $\text{Mg}[\text{HTi}(\text{OC}_4\text{H}_9)_6]_2$ in n-butanol.

The mixture was stirred and heated under nitrogen to a temperature of 200° C. During the first, or alcoholysis stage of the reaction, butanol is evolved and collected. After sixty minutes, the reaction temperature was increased over a forty minute period to 280° C. A vacuum was then rapidly applied and within five minutes the pressure was reduced to less than 0.15 mm. of mercury. The residual polymer was stirred at this temperature and pressure for sixty minutes during which time the viscosity of the melt increased rapidly until the polymer was wrapping about the stirrer in a ball. The product from this second, or melt phase, stage of the polymer preparation was cooled, removed from the flask and found to have an inherent viscosity of 1.68. The final polymer contained 82.5 percent by weight of the copolyether, and for further evaluation the polymer was extracted with ether in a Soxhlet extractor for six hours to remove the residual Aroclor 5442.

Samples of the extracted elastomer were pressed into film and the degree of set determined on stretched samples at various temperatures using the test method already described. The results are given numerically below.

Temperature, ° C.....	0	10	15	20	25	30
Percent Set.....	47	40	37	30	27	20

Example 2

The procedure of Example 1 was repeated, except that the polyether used was prepared entirely from tetrahydrofuran and had a number average molecular weight of 3300. The degree of set at different temperatures was determined for stretched film samples and these figures are given below.

Temperature, ° C.....	0	10	15	20	25	30
Percent Set.....	140	123	93	60	33	27

A comparison of these two examples demonstrates the improvement effected by the use of copolyethers in the preparation of elastomers. The product of Example 2 is an elastomer prepared from a homopolyether and that of Example 1 is an elastomer prepared from a copolyether. The degree of set determined on the polymer of Example 1 is considerably less than the set of the polymer of Example 2. This improvement is particularly evident at temperatures below 25° C. The critical set temperature of the polymer of Example 2 is 25° C., while the polymer of Example 1 has a definite critical set temperature of approximately 17° C. The difference in behavior is more evident if the results are plotted graphically. The subject matter of Examples 2, 6, 7 and 8 is more fully described and claimed in our copending application Serial No. 215,768, filed on August 9, 1962, and is included herein for comparative purposes.

Example 3

The procedure of Example 1 was used to prepare an elastomeric polyester from a mixture of 7.25 g. (0.0261 mole) of dibutyl terephthalate, 6.24 g. (0.0433 mole) of trans-1,4-cyclohexanedimethanol, 24.0 g. (0.0089 mole) of a polyether of molecular weight 2700 prepared from a 90 mole percent mixture of tetrahydrofuran and a 10 mole percent mixture of 8-oxabicyclo[4:3:0]nonane, 0.6 g. of dilauryl thiodipropionate, 12 g. of Aroclor 5442 and 0.6 ml. of a 21 percent solution of $\text{Mg}[\text{HTi}(\text{OC}_4\text{H}_9)_6]_2$ in n-butanol. The final polymer had an inherent viscosity of 1.61 and contained 80 percent by weight of the copolyether. A sample was extracted for six hours with ether to remove residual Aroclor, a film was pressed and the percentage set at various temperatures determined.

Temperature, ° C.....	0	10	15	20	25	30
Percent Set.....	40	37	30	23	17	13

It can be seen that a copolyether containing only 10 mole percent of 8-oxabicyclo[4:3:0]nonane is effective in markedly reducing the critical set temperature. It is also possible to achieve beneficial results by using mixtures of copolyether with the homopolyether prepared from tetrahydrofuran, poly(tetramethylene glycol). The effect is not to eliminate the critical set temperature but to depress it to sufficiently low temperatures that no problem is encountered in using the elastomer under normal conditions. This is demonstrated in the following example.

Example 4

The preparative procedure of Example 1 was used to prepare an elastomeric polyester from a mixture consisting of 7.25 g. (0.0261 mole) of dibutyl terephthalate, 6.24 g. (0.0433 mole) of trans-1,4-cyclohexanedimethanol, 17.6 g. (0.00765 mole) of poly(tetramethylene glycol) of molecular weight 2300 and 6.4 g. (0.00168 mole) of a copolyether, molecular weight 3800 prepared from a mixture containing 75 mole percent of tetrahydrofuran and 25 mole percent of 8-oxabicyclo[4:3:0]nonane, 0.6 g. of dilauryl thiodipropionate, 12 g. of Aroclor 5442, and 0.6 ml. of a 21 percent solution of $\text{Mg}[\text{HTi}(\text{OC}_4\text{H}_9)_6]_2$ in n-butanol.

The final polymer contained 80 percent by weight of the mixture of poly(tetramethylene glycol) and copolyether and had an inherent viscosity of 1.81. An extracted sample was pressed into film and the degree of set measured at various temperatures. These measurements are reported below.

Temperature, ° C.....	0	10	15	20	25	30
Percent Set.....	73	47	30	20	17	13

It can be seen that the critical set temperature is approximately 13° C. This is a much lower value than that for the polymer of Example 2 which was prepared entirely from poly(tetramethylene glycol).

plication Serial No. 215,768 filed on August 9, 1962, and is included herein for comparative purposes.

It can readily be seen that the presence in the elastomeric polyester of a copolyether containing as little as 5 mole percent of a modifier depresses the critical set temperature of the polyester markedly and improves the elongation. In addition, higher molecular weight modified polyethers can be used which results in the formation of elastomeric polyesters of higher softening temperature.

Ex.	Polymer Composition			Polymer Inherent Viscosity	Percent Set at Various Temperatures						Critical Set Temp., ° C.	Percent Elongation
	Weight Percent Polyether or Co-polyether	Molecular Weight of Polyether or Co-polyether	Mole Percent 8-oxabicyclo[4:3:0]nonane		0° C.	10° C.	15° C.	20° C.	25° C.	30° C.		
6.....	66	2,700	0	1.65	140	130	110	90	37	23	25	400
7.....	77	2,300	0	1.83	120	87	67	20	17	13	20	475
8.....	80	3,000	0	1.87	130	120	100	87	37	23	25	550
9.....	66	2,600	50	1.66	93	87	40	30	23	20	10	600
10.....	70	2,500	25	1.72	47	40	33	27	20	13	<0	650
11.....	80	2,500	5	1.90	47	30	20	17	17	17	10	700
12.....	85	4,800	20	1.72	43	37	30	27	20	17	<0	800
13.....	87.5	4,400	15	1.97	47	37	30	27	20	17	12	900
14.....	89	5,500	15	2.06	47	37	37	27	27	20	17	900
15 ^a	80	3,000	7.5	2.11	60	37	23	13	10	11	11	725
16 ^a	85	4,900	7.5	1.87	40	30	30	27	23	17	5	975
17 ^b	67	3,000	15	1.71	53	43	37	27	27	23	17	650
18 ^c	82.5	3,000	6	2.17	70	43	23	20	17	17	12	800
19 ^d	82.5	4,000	12	1.79	37	30	27	20	17	17	5	800

^a50/50 mixture of poly(tetramethylene glycol) and the copolyether containing 15 mole percent of 8-oxabicyclo[4:3:0]nonane.

^bPrepared with 1,4-cyclohexanedimethanol containing 70 percent trans isomer.

^c25/75 mixture of poly(tetramethylene glycol) and the copolyether containing 8 mole percent of 8-oxabicyclo[4:3:0]nonane.

^dCopolyether prepared from tetrahydrofuran and 3-methyl-8-oxabicyclo[4:3:0]nonane.

This material was also spun into fibers having the following properties:

Tenacity, g./d.	0.372
Elongation, percent	620
Secant modulus at 100% extension, g./d.	0.038
Recovery from 400% extension, percent	95.5
Recovery from 600% extension, percent	92.1
Permanent set after holding at 150% extension, 16 hr., percent	17
Sticking temperature, ° C	104-119

Example 5

The procedure of Example 1 was repeated using a mixture of 9.12 g. (0.0328 mole) of dibutyl terephthalate, 8.05 g. (0.0558 mole) of trans-1,4-cyclohexanedimethanol, 22.1 g. (0.0098 mole) of a polyether synthesized from a mixture of 85 mole percent tetrahydrofuran and 15 mole percent 8-oxabicyclo[4:3:0]nonane and having a number average molecular weight of 2300, 12 g. of Aroclor 5442, 0.6 g. of dilauryl thioldipropionate and 0.6 ml. of a 21 percent solution of Mg[HTi(OC₄H₉)₆]₂ in n-butanol.

The final polymer contained 74.5 percent by weight of the copolyether and had an inherent viscosity of 1.7. An ether extracted sample was pressed into film and the degree of set measured at various temperatures. The results are as follows:

Temperature, ° C.....	0	10	15	20	25	30
Percent Set.....	47	40	33	27	23	20

Samples of this film also showed an elongation to break of 900 percent and an elastic recovery from 400 percent extension of 92 percent.

The table in column 10 summarizes the results obtained with several different compositions prepared in accordance with our invention and includes for comparison three more compositions (Examples 6, 7, 8) which were prepared from the homopolyether poly(tetramethylene glycol). The subject matter of Examples 2, 6, 7 and 8 is more fully described and claimed in our copending ap-

As indicated above and by the examples, the final polyesters of our invention may contain 50 to 93 weight percent of the copolyether but preferably the weight percent of polyether should be in the range of 75 to 87 percent. The molecular weight of the polyether can be in the range of 1000 to 10,000 but preferably is in the range 2200 to 5000.

The use of the copolyether glycol as hereinabove set forth results in other advantages as a consequence of the improved set properties. One is that higher molecular weight copolyethers can be utilized than is the case with unmodified poly(tetramethyleneglycol). When unmodified polyether is employed critical set temperatures above 25° C. are found in the elastomeric polyester whenever the molecular weight of the polyether is above 3000. In contrast to this, when copolyether glycols are employed in accordance with the invention, molecular weights as high as 10,000 can be used and the elastomeric polyesters have set transition temperatures lower than 20° C.

Since it is possible to use polyethers with high molecular weights, it then becomes possible to incorporate larger amounts of the copolyether into the elastomeric polyester without seriously lowering the melting point. In the case of poly(tetramethylene glycol) molecular weights above 3000 cannot be readily used, so that 80 percent by weight of the polyether is about the maximum amount that can be incorporated into a polyester without lowering the melting point below a useful level. On the other hand, when copolyether glycols are employed in accordance with our invention, much higher molecular weights can be used, hence a higher weight percent of the copolyether can be incorporated into the polyester. Fibers melt spun from these elastomeric copolyesters containing the copolyether are found to have higher elongations and an improved recovery from high elongation as well as a much reduced critical set temperature as compared to analogous compositions containing only the homopolyether of poly(tetramethylene glycol), as the ether glycol.

The importance of a low critical set temperature is perhaps not at first apparent. Therefore, consider a fiber prepared from an elastomer with a critical set tem-

perature of 30° C.—a value somewhat above room temperature. When this fiber is stretched and released, it is found to retain a considerable portion of its stretched length (i.e., it has a high degree of set) and does not return to its original length. On warming the fiber above 30° C., it loses its set and returns to essentially its original length. Garments incorporating such elastomeric fibers would show an apparent permanent distortion each time they were stretched unless they were used at temperatures above 30° C.

In the case of fibers from elastomers with critical set temperatures near room temperature, the fibers usually show a smooth return to their original length. However, should the air temperature be low, the fibers would show a high degree of set. If these fibers are incorporated into a garment, the garment would prove satisfactory in normal use, but there exists a good chance that such a garment on display will appear to have poor elastic properties when examined by a customer. Thus, it is important from a sales viewpoint to reduce the critical set temperature.

In addition, it is obvious that low critical set temperatures in elastomers will enable them to be used for various applications at temperatures lower than room temperature, such as protective elastic coverings, elastic coatings for paper and the like, conformable elastic films, flexible tubing, wire coatings, etc. In all these applications, high elastic deformation and recovery are essential properties for elastomeric materials.

In addition to the unusual combination of physical properties obtainable in filaments, fibers and yarns produced from the compositions of our invention, as described above, such yarns are also characterized by the fact that they have high hydrolytic stability. Consequently, garments fabricated from yarns produced from compositions of our invention are capable of being subjected to the most extreme of laundering conditions with no deleterious effects. This contrasts sharply with the behavior of polyester elastomeric yarns of the prior art as described in the aforementioned Textile Industries' article of August 1961 referred to above.

Another property of extreme importance in elastomeric yarns is stress decay or stress relaxation. As also stated in the above-mentioned Textile Industries' article of August 1961, a low stress relaxation is important, otherwise elastic garments such as foundation garments will exert less and less pressure upon the wearer's body the longer they are worn.

The fibers, yarns and filaments of our polyester compositions show a low stress decay or stress relaxation or, as it is commonly expressed, the filaments lose a small percentage of the original stress required to extend them to a given elongation. As the test is usually run, the fiber is stretched to a 300 percent elongation and held at this elongation while the tension on the fiber is measured by means of a spring balance as a function of time. The decrease in stress during the test period is expressed as a percentage of the stress originally necessary to draw the fiber to the 300 percent elongation.

The fibers prepared from our elastomeric compositions show a stress relaxation behavior very similar to rubber and superior to the spandex elastomeric fibers. The Federal Trade Commission defines spandex as a term applied to manufactured fiber in which the fiber-forming substance is a long chain of synthetic polymer comprised of at least 85% of a segmented polyurethane. The following table illustrates this fact.

Percent stress lost after 2½ minutes of fibers elongated 300 percent

Fiber:	Percent stress lost
Spandex	37-40
Rubber	20
Fibers of instant invention	16-22

It is desirable for elastomeric yarns to possess a high thermal stability. This is necessary so that garments containing the elastomeric yarns can be laundered, machine dried and ironed with no special precautions and yet suffer no loss of properties. As described in our copending application U.S. Serial No. 166,155, filed January 15, 1962, we have found that such thermal stability is imparted to the elastomeric yarns by incorporating therein small (0.01 to 5 percent by weight) amounts of certain 2,4,6-trialkylated phenols. These may be used alone but unusually high thermal stabilities are obtained if the phenol is used in combination with esters or polyesters derived from thiodipropionic acid, such as dilauryl thiodipropionate or a polyester prepared from thiodipropionic acid and ethylene glycol.

The phenols of particular interest are 2,6-di-n-dodecyl-4-methylphenol, 2,6-di(1-methylheptadecyl)-4-methylphenol and the like. Fibers containing such phenolic stabilizers have the added advantage that they do not develop a yellow color on exposure for extended periods of time to light and the atmosphere. A fiber which does show this property (termed gas fading or yellowing) suffers from a very serious disadvantage in the textile industry.

The introduction of the stabilizer composition into the fiber can be accomplished most simply by introducing the reagents into the reaction vessel together with the other reagents. A second method is to add the stabilizers to the elastomeric polymer at the completion of polymerization. A third would involve adding the stabilizers immediately before spinning or extruding. This addition may be accomplished by dusting the stabilizers onto the polymer or by mixing a "master batch" of stabilizer into the regular polymer. This master batch is prepared by milling a high concentration of the stabilizer into a low melting elastomeric composition. The master batch is then chopped, blended in the proper proportions with the base polymer, and the blend spun, molded or extruded.

In addition pigments and other coloring materials, de-lustering agents and anti-sticking agents may be added to the polymer during synthesis or prior to shaping into final form. Such may be added by incorporating said materials in a master batch and adding to the polymer prior to shaping portions of the master batch.

Example 20

A master batch is prepared as follows: The dispersing medium for the master batch is a polymer prepared from dimethyl terephthalate, 1,4-cyclohexanedimethanol and a copolyether glycol of molecular weight 3500 prepared from a mixture of tetrahydrofuran containing 8 mole percent of 8-oxabicyclo[4:3:0]nonane, the final elastomeric copolyester containing 82.5 percent by weight of the copolyether glycol. Two hundred grams of this polymer was placed on the rolls of a small rubber rolling mill, the rolls being maintained at 150° C. When the polymer had become properly distributed as a band on the rolls, 12.5 grams of dilauryl thiodipropionate, 50 grams of rutile titanium dioxide and 25 grams of 2,6-di(1-methylheptadecyl)-p-cresol was added in increments. The band was stripped from the rolls, broken and replaced on the rolls until thorough mixing was insured. It was then removed and broken into small pieces. This material, known as the master batch, was blended with 2200 grams of the polymer prepared as described in Example 3. The final mixture was melt spun into fibers which contained 2 percent by weight titanium dioxide, 0.5 percent by weight of dilauryl thiodipropionate and 1 percent by weight of 2,6-di(1-methylheptadecyl)-p-cresol.

The fibers from this spinning were exposed to the air at 125° C. and the fiber properties determined from samples withdrawn periodically. The fibers stabilized in the manner described above still retained more than 50 percent of their original tenacity and more than 50 percent

of their original elongation after 200 hours. As showing the efficacy of employing stabilizers, when no stabilizer was added to the polymer before spinning, the final fibers retained less than 25 percent of their original physical properties after 15 hours heating in air at 125° C.

In addition, the stabilized fibers were exposed in a fume or gas-yellowing test according to Procedure No. 23-1957 of the American Association of Textile Chemists and Colorists. No yellow color developed after three cycles of this test which is considered to be equivalent to 18 months of wear. Such a behavior is given a rating of 5 in this test—the highest rating which it is possible to assign.

Example 21.—Continuous melt phase polymerization

The polyester compositions of our invention are conveniently prepared commercially by a continuous melt phase polymerization process.

The drawing of the figure designated FIGURE 1 of our copending application Serial No. 166,155 is a simplified illustration in the nature of a flow sheet showing schematically one form of apparatus in which the polymers of our invention can be prepared.

The polyether used was a mixture of two parts by weight of the copolyether prepared from tetrahydrofuran and 8-oxabicyclo[4:3:0]nonane in which 9:3 mole percent of the latter compound was present and the copolyether had a number average molecular weight of 3750 and one part by weight of poly(tetramethylene glycol) of number average molecular weight 3400 and having a sharp molecular weight distribution. The final mixture had an average molecular weight of 3600 and contained an average of 6.1 mole percent of 8-oxabicyclo[4:3:0]nonane modifier. The reagents were mixed batchwise, each batch consisting of similar proportions of reactants, as, for example, 9750 grams (2.71 moles) of the copolyether-poly(tetramethylene glycol) mixture described hereinabove, 1585 grams (8.18 moles) of dimethyl terephthalate, 2000 grams (13.9 moles) of trans-1,4-cyclohexanedimethanol, 114 grams of a 21 percent solution of $Mg[HTi(OC_4H_9)_6]_2$ in n-butanol, and 350 grams (3 percent by weight of the final polymer) of dilauryl thiodipropionate. This mixture was melted by heating to 140° C., stirred and fed at a rate of 17 pounds per hour into a column equipped with plates which serves as a prepolymerizer. The prepolymerizer column was heated to 220° C. by means of hot oil introduced into an external jacket and the pressure in the column generated by the evolved methanol was regulated by a pressure regulator at about 10 p.s.i.g. (the term p.s.i.g. is herein used to indicate pounds per square inch gauge). The molten reagents covered the plates and flowed down the column by passing through overflow pipes from each plate onto the plate beneath. At the bottom of the prepolymerizer, the reaction product was delivered by a pump through a heated tube to a polymerizer column in which the final polymer was formed. This column which serves as a reactor was heated to 278° C. by a jacketed hot oil system and maintained under vacuum by two independent vacuum systems operating through the manifolds leading from the column. The column was divided into two sections separated by a liquid seal in which molten polymer served as the liquid seal in which molten polymer served as the liquid. The upper section above the liquid seal was maintained at a pressure of 1 to 2 mm. of mercury and the lower section was maintained at a pressure of 0.2 mm. of mercury. The low molecular weight material delivered to this polymerizer column was distributed through the upper section so as to expose the maximum surface to the vacuum, and then the material passed through the liquid seal into the lower section. In this lower section, the polymer flowed over a series of sloping heated baffle plates which slope in alternate directions as it descended through the column. During the descent, the polymer increased rapidly in viscosity. At the bottom of the column a pump

was used to remove the polymer from the column and feed it into a quenching bath of water.

The final polymer had an inherent viscosity of 2.0 to 2.1 and contained 84 percent by weight of the polyether mixture. This material was melt extruded at 260° C. into continuous filament which was found to have the following fiber properties:

Denier	604
Tenacity, g./d.	0.26
Elongation, percent	570
Secant modulus at:	
30% extension, g./d.	0.025
100% extension, g./d.	0.040
Recovery from 400% extension, percent	95.8
Permanent set after holding at 150% extension, 16 hr., percent	17
Sticking temperature, ° C.	135-157
Melting point, ° C.	220-230

The elastomeric polyester filaments, fibers and yarns of this invention are characterized by a high melting point, a high degree of elongation and recovery from stretch, and a high strength. Fabrics made from these yarns will, therefore, be capable of an extension from two to five times their original length and yet may be treated in much the same way as a normal synthetic fabric. That is, they may be washed and dried in commercial or home automatic equipment and they may be dry cleaned and ironed without special precautions. Furthermore, the yarns of this invention are readily dyed and show a high resistance to degradation by oxidation, exposure to light, soap, perspiration or greases and many common chemicals.

It should be emphasized that the elastomeric polyesters of the instant invention are particularly characterized by retaining the above mentioned advantageous elastomeric properties at temperatures below room temperature that is below about 24° C. Filaments, fibers and yarns of our polyester compositions retain a high degree of elongation and recovery from stretch at temperatures within the range of 0° C. to 20° C. Thus they have the additional and valuable advantage of retaining their advantageous properties under conditions where the commonly used elastomer fail to perform satisfactorily.

Therefore, it is apparent that a yarn or film of this type which has high extensibility and elastic recovery, together with the other advantageous properties described above, will be useful in the fabrication of many articles, such as brassieres, girdles, surgical hosiery, men's braces, bathing suits, stocking tops, suspenders, garters, pajamas, panties, shorts, sweaters, jackets, ski togs, dresses, blouses, shirt collars, skirts, caps and hats, gloves, tapes and ribbons, laces, belting, shoe fabrics, slip covers, upholstery, elastic bandages, hair nets, covers for jars and dishes, ropes and balls, and many other products.

A brief discussion of a few of these uses will serve to emphasize the advantages of the elastomeric yarns of this invention. In the case of foundation garments, the fabrics woven from the subject yarns have a good elongation, a high elastic recovery and a high strength. Accordingly, fabrics will exert substantial pressure against the body of the wearer. Foundation garments can be constructed which have the desired retaining power and yet are lighter in weight and bulk and more comfortable to wear than those now available. Because of the natural resistance to greases, to alkaline soaps and detergents, and hot water, the garments may be washed and dried in a conventional manner with no deleterious effect on their life expectancy.

The resistance of the fabrics to grease, ointments and many chemicals makes the subject elastomeric polymers particularly useful for elastic bandages, and surgical hosiery. Again the high strength can be used to reduce the weight and bulk of the bandages and hosiery, thereby increasing the comfort of the patient.

Their use in bathing suits, slip covers and upholstery fabrics depends upon the combination of high elasticity

and strength, ready dyeability, and good resistance to sunlight, soaps and detergents, etc. Thus bathing suits or slip covers, objects which are necessarily gaily colored, need be constructed in only a few sizes and yet, because of the high elasticity of the fabric, these few sizes can accommodate a wide variety of shapes and sizes with no alterations in the original construction. This would result in a considerable simplification in the manufacture of these products.

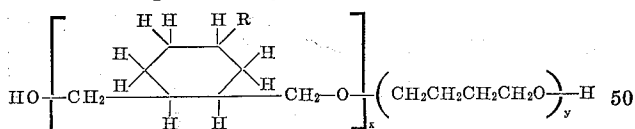
While the invention has been described in terms of an elastic yarn, it will be understood that the characteristics of the subject polyester can find uses other than in yarns. Among such uses, there may be mentioned elastic coatings for paper and the like, fabric coatings, conformable elastic films, heat-shrinkable closures for bottles and the like, safety glass interlayers, flexible tubing, coatings for wire, and many other products.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

We claim:

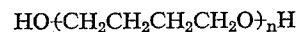
1. A highly elastic fiber-forming linear polyester of equimolar proportions of constituents consisting essentially of dicarboxylic acid constituents (A) and glycol constituents (B) and (C), said linear polyester having an inherent viscosity above 1.4 as measured in a mixture of 60% phenol plus 40% tetrachloroethane at 25° C., having a crystalline melting point greater than 150° C. and being capable of forming highly elastic fibers having a tenacity of at least about 0.26 gram per denier and having no more than about a 22% decrease, after 2.5 minutes, in the stress required to elongate such fibers by 300%, wherein said dicarboxylic acid and glycol constituents (A), (B) and (C) are as follows:

- (A) a dicarboxylic acid in which the carboxy radicals are directly attached to a hexacarboxylic ring,
- (B) a glycol selected from the group consisting of the cis and trans isomers of 1,4-cyclohexanedimethanol,
- (C) a glycol selected from the group consisting of:
 - (C-1) a copolyether glycol having two different repeating units in its molecular structure which is represented by the following formula:



wherein R represents a member selected from the group consisting of a hydrogen atom and a methyl radical, x and y each represents an integer greater than zero such that x is less than y and the sum of x plus y is from 14 to 130 and the repeating units are distributed in a random manner in each molecule of said copolyether glycol, and mixtures of (C-1) with

(C-2) a polytetramethylene ether glycol having a molecular structure represented by the following formula:



wherein n represents an integer of from 14 to 70, the combined amount of glycol constituent (C-1) and glycol constituent (C-2) being such that from 5 to 100 mole percent of said combined amount is said constituent (C-1), the combined amount of glycol constituents (C-1) and (C-2) being from 50 to 93% by weight of said linear polyester and the amount of glycol constituent (B) is at least 50 mole percent of the sum of the glycol constituents (B), (C-1) and (C-2).

- 2. A polyester as defined by claim 1 wherein said constituent (A) is terephthalic acid.
- 3. A polyester as defined by claim 1 wherein said constituent (A) is 4,4'-sulfonyldibenzoic acid.
- 4. A polyester as defined by claim 1 wherein said constituent (A) is 2,6-naphthalenedicarboxylic acid.
- 5. A polyester as defined by claim 1 wherein said constituent (A) is trans 1,4-cyclohexanedicarboxylic acid.
- 6. A polyester as defined by claim 1 wherein said constituent (A) is diphenic acid.
- 7. A polyester as defined by claim 1 wherein said combined amount of constituent (C-1) and (C-2) is from 75 to 87% by weight of said polyester and the sum of x plus y is from 30 to 70.
- 8. A polyester as defined by claim 1 wherein R in said constituent (C-1) is hydrogen.
- 9. A polyester as defined by claim 1 wherein R in said constituent (C-1) is methyl.
- 10. A polyester as defined by claim 1 containing none of said constituent (C-2).
- 11. A fiber of the polyester of claim 1.
- 12. A fiber of the polyester of claim 2.
- 13. A fiber of the polyester of claim 7.
- 14. A fiber of the polyester of claim 8.
- 15. A fiber of the polyester of claim 10.

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