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(19) (CA) **CANADIAN PATENT** (12)

(54) **Nonlinear Optical Medium With a Stable Noncentrosymmetric Polymeric Structure**

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(57) **24 Claims**

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ABSTRACT OF THE DISCLOSURE

This invention provides nonlinear optical media which have a stable noncentrosymmetric array of side chain polymer molecules, such as an electric field poled and stabilized medium of a 50/50 copolymer of
N-methyl-4-[2-(4-nitrophenyl)ethenyl]phenylamino-2-ethyl
2-methyl-2-propenoate and
4-[2-(4-nitrophenyl)ethenyl]phenylthio-2-ethyl
2-methyl-2-propenoate.

BACKGROUND OF THE INVENTION

It is known that organic and polymeric materials with large delocalized π -electron systems can exhibit nonlinear optical response, which in many cases is a much larger response than by inorganic substrates.

In addition, the properties of organic and polymeric materials can be varied to optimize other desirable properties, such as mechanical and thermoxidative stability and high laser damage threshold, with preservation of the electronic interactions responsible for nonlinear optical effects.

Thin films of organic or polymeric materials with large second order nonlinearities in combination with silicon-based electronic circuitry have potential as systems for laser modulation and deflection, information control in optical circuitry, and the like.

Nonlinear optical properties of organic and polymeric materials was the subject of a symposium sponsored by the ACS division of Polymer Chemistry at the 18th Meeting of the American Chemical Society, September 1982. Papers presented at the meeting are published in ACS Symposium Series 233, American Chemical Society, Washington, D.C., 1983.

Of more specific interest with respect to the present invention embodiments is prior art relating to side chain liquid crystalline polymers, such as the five articles published on pages 275-368 of "Polymeric Liquid Crystals", edited by A. Blumstein (Plenum Publishing Corporation, New York 1985).



Makromol, 179, 2541 (1978) by H. Finkelmann et al describes a model consideration for liquid crystalline polymers with side chain biphenyl groups as mesogenic entities.

J. Polym. Sci., 19, 1427 (1981) by Paleos et al describes the synthesis of liquid crystalline polymers which are prepared by the interaction of poly(acryloyl chloride) with mesogenic compounds such as p-aminobiphenyl.

Other publications which describe polymers with side chain induced crystallinity include Polymer, 25, 1342 (1984);
10 Eur. Polym. J., 21, No. 7 645 (1985); Polymer, 26, 615 (1985);
and references cited therein.

There is continuing interest in the theory and practice of polymers which are characterized by an oriented state of comb-like side chain structures.

There is also an increasing research effort to develop new nonlinear optical organic systems for prospective novel phenomena and devices adapted for laser frequency conversion, information control in optical circuitry, light valves and optical switches. The potential utility of organic
20 materials with large second order and third order nonlinearities for very high frequency application contrasts with the bandwidth limitations of conventional inorganic electrooptic materials.

Accordingly, it is an object of this to provide organic nonlinear optical media which exhibit a high level of nonlinear optical response.

It is another object of this invention to provide nonlinear optical media which have a stable noncentrosymmetric structure of side chain polymer molecules, and to provide a process for their production.

It is a further object of this invention to provide optical switch and light modulator devices with a transparent polymeric optical component comprising a stable orientation of polymer molecules with pendant side chains that exhibit second order nonlinear optical susceptibility β .

10 Other objects and advantages of the present invention shall become apparent from the accompanying description and example.

DESCRIPTION OF THE INVENTION

One or more objects of the present invention are accomplished by the provision of a process for producing a second order nonlinear optical medium having a stable
5 noncentrosymmetric orientation of polymer molecules, which process comprises (1) heating a film of a polymer with pendant side chains to a temperature of at least about the polymer glass transition temperature (T_g); (2) subjecting the polymer medium to an external electric field to induce
10 noncentrosymmetry in the polymer medium by molecular orientation of the polymer side chains which exhibit second order nonlinear optical susceptibility; and (3) cooling the noncentrosymmetric polymer medium to a temperature between about T_g and 20°C to solidify the polymer medium while
15 maintaining the electric field effect and the polymer molecular orientation, wherein the temperature cycle between T_g and 20°C is over a period of time sufficient to achieve ordered thermal relaxation and stabilization of the induced second order properties in the oriented polymer medium.

20 The temperature cycle in step (3) of the process typically is over a period between about thirty minutes and 300 hours.

The glass transition temperature (T_g) of the polymer employed in the process is in the range between about 60°C -
25 250°C .

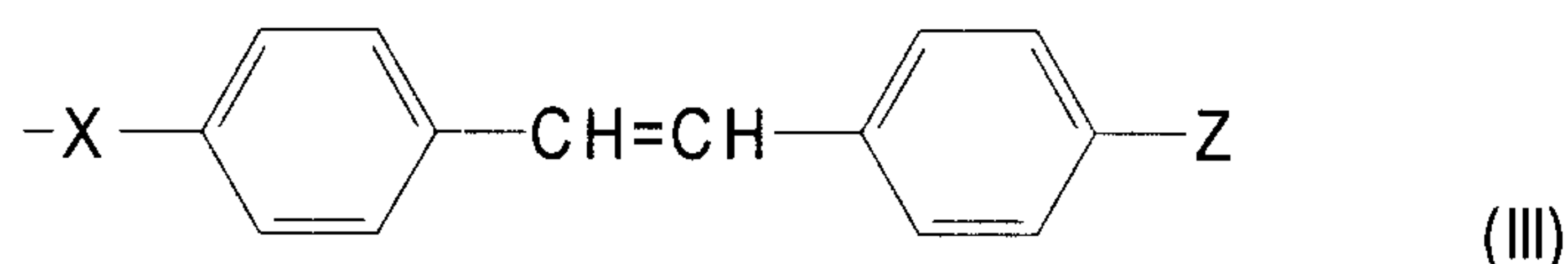
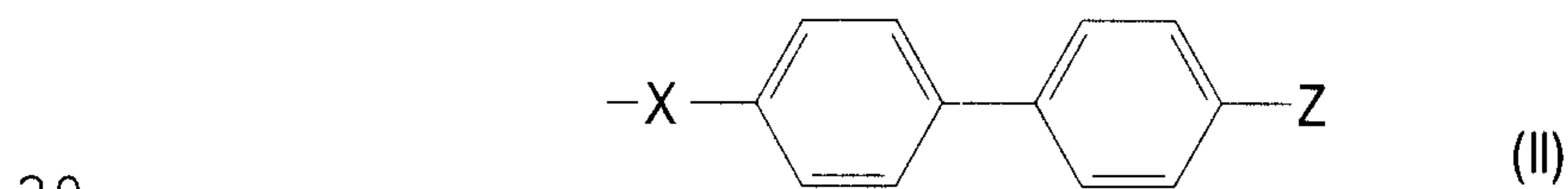
Polymers which are suitable for the process include those which are characterized by a recurring monomer unit corresponding to the formula

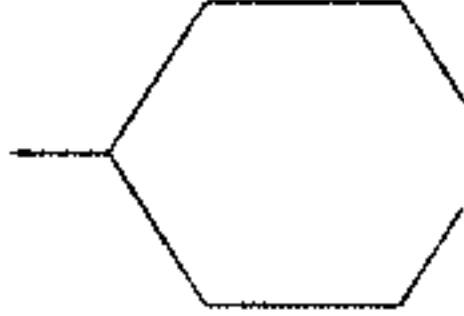
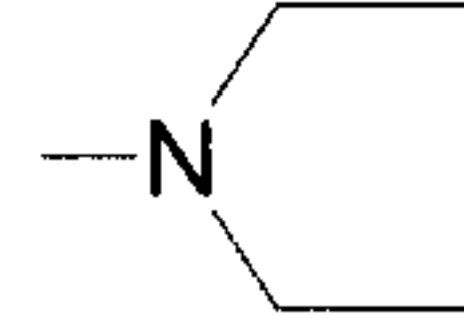


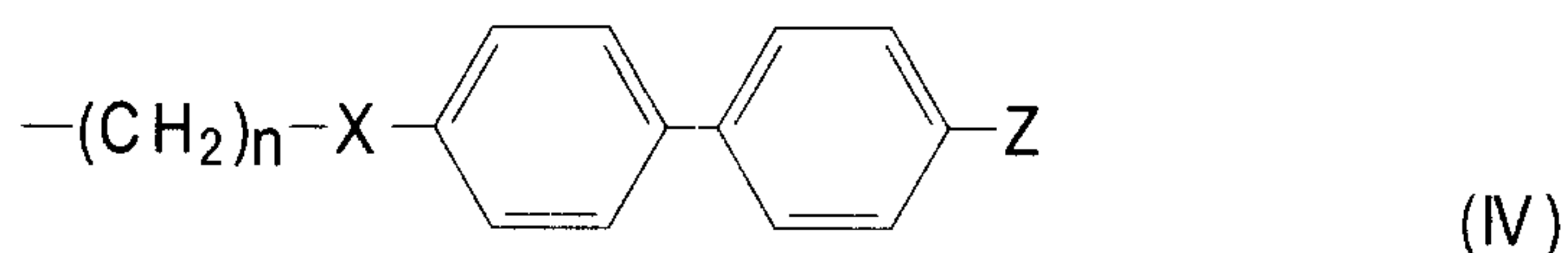
where P' is a polymer main chain unit, S' is a side chain flexible spacer group having a linear chain length of about 1-20 atoms, M' is a side chain pendant group which exhibits second order nonlinear optical susceptibility β , and where the recurring monomeric unit comprises at least 20 weight percent of the polymer, and the polymer has a glass transition temperature above about 60°C.

Preferred polymers are those in which the pendant M' group in the polymer side chain is a polar organic structure that has a dipole moment which is greater than about 4 debye units.

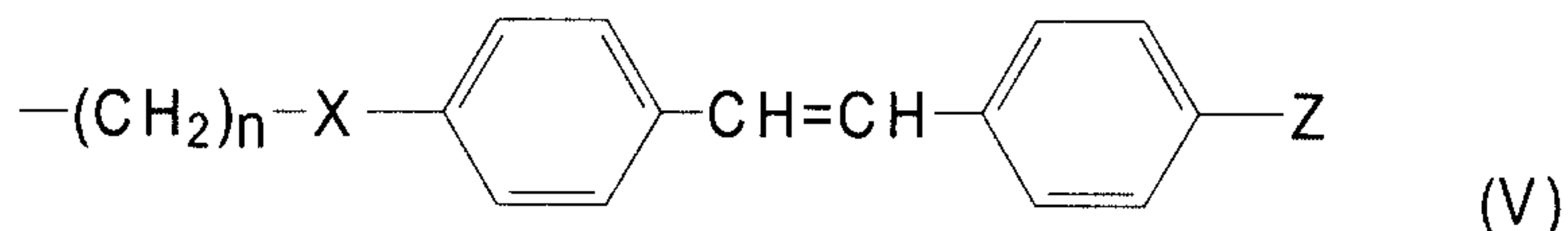
Illustrative of a pendant M' group in the polymer side chain is any one of the following structures:



where X is -O-, -S-, -NR-,  or ; R is hydrogen or a C₁-C₄ alkyl substituent; and Z is -NO₂, -CN, -CF₃,
 25 -SO₃CF₃, ---CH=C(CN)--- or ---C(CN)=C(CN)--- ,



or



5

where n is an integer between about 2-12, and X and Z are as defined above. The $-(\text{CH}_2)_n-$ radical corresponds to S' in the polymer formula.

The polymer main chain can have a structure such as
 10 polyvinyl, polysiloxane, polyoxyalkylene, polyamide, polyester, and the like.

The side chain polymers illustrated above can be synthesized by procedures described elsewhere.

In another embodiment this invention provides a
 15 process for producing a second order nonlinear optical medium having a stable noncentrosymmetric molecular orientation of polymer molecules, which process comprises: (1) heating a film of a polymer with pendant side chains to a temperature in the range between about the polymer glass transition temperature
 20 (T_g) and 30°C ; (2) subjecting the heated polymer medium to an external electric field to induce noncentrosymmetry in the polymer medium by molecular orientation of the polymer side chains which exhibit second order nonlinear optical susceptibility; and (3) maintaining the noncentrosymmetric
 25 polymer medium in solid form in the temperature range between about T_g and 30°C while maintaining the electric field effect and the polymer molecular orientation, wherein the temperature

cycle between T_g and 30°C is over a period of time between about thirty minutes and 300 hours sufficient to allow ordered thermal relaxation so as to stabilize the induced second order properties in the oriented polymer medium.

- 5 The heating of the polymer medium in the above described process steps typically is in the range between T_g and $0.5 T_g$ ($^\circ\text{C}$).

The temperature cycle in step (3) of the process embodiment is over a period between about 0.1-60 hours.

- 10 The polymer film in the process has a thickness between about 1.0-1000 microns.

In any of the process embodiments the external field is applied to the polymer film with a pair of electrodes having an operating voltage range between about 10-1000 V/ μm .

- 15 In another embodiment this invention provides a second order nonlinear optical medium comprising a stable noncentrosymmetric orientation of polymer molecules, wherein the polymer has side chains which exhibit second order nonlinear optical susceptibility, and wherein there is less
20 than about 10 percent loss of second order nonlinear optical activity exhibited by the medium when the medium is maintained at 50°C for one year.

- In a further embodiment this invention provides an optical light switch or light modulator device with a polymeric
25 second order nonlinear optical component comprising a noncentrosymmetric medium of oriented polymer molecules, wherein the polymer has side chains which exhibit second order nonlinear optical susceptibility, and wherein there is less than about 10 percent loss of second order nonlinear optical



activity exhibited by the optical medium when the medium is maintained at 50°C for one year.

A present invention nonlinear optical device can be achieved by constructing one of the optical devices described in the technical literature, except that a present invention side chain polymer medium is utilized as the nonlinear optical component.

Optical harmonic generating devices are described in Science, 216 (1982); and in United States Patent Numbers 3,234,475; 3,395,329; 3,694,055; 3,858,124; and 4,536,450.

An optical interferometric waveguide gate device is described by A. Lattes et al in IEEE J. Quantum Electronics, QE-19(11), 1718 (1983).

A wide-band electrooptical guided-wave analog-to-digital converter device is described by R.A. Becker et al in proceedings of the IEEE, 72(7), 802 (1984).

Optical multiplexer-demultiplexer devices are described in United States Patent Numbers 3,532,890; 3,755,676; 4,427,895; 4,455,643; and 4,468,776.

Optical bistable devices are described in United States Patent Numbers 4,515,429 and 4,583,818; and by P.W. Smith et al in Applied Physics Letters, 30(6); 280 (1977) and in IEEE Spectrum, June 1981. Optical parametric devices are described in United States Patent Numbers 3,371,220; 3,530,301; and 3,537,020.

X⁽²⁾ Relaxation Model

A theoretical model for the X⁽²⁾ relaxation of solid side chain polymers can be derived from a modified version of the William-Landel-Ferry (WLF) equation, and parameterized for

temperatures below the glass transition temperature (T_g) of polymethyl methacrylate.

The empirical WLF equation is based on a free volume theory that assumes a linear dependence between the fractional
5 free volume and temperature:

$$\log \frac{\tau(T)}{\tau(T_0)} = \frac{-C_1(T-T_0)}{C_2 + (T-T_0)} \quad (1)$$

where τ is the relaxation time, T_0 is an arbitrary reference temperature such as the glass transition temperature (T_g), and C_1 and C_2 are constants having values of 17 and 52, respectively, which nominally are independent of polymer
10 structure.

The WLF equation is valid for many polymer substrates above T_g . The WLF equation is not valid below T_g because the non-equilibrium phase of a poled polymer medium below T_g is not factored into the WLF equation.

15 K.C. Rusch [J. of Macromol. Sci. Phys., B2(2), 179(1968)] extended the validity of the free volume concept to the less than T_g region and derived a modified version of the WLF equation. It is assumed that in the glassy polymer state the free volume consists of an equilibrium phase v_f and a non-
20 equilibrium phase w_f . If $v(T)$ is the total free volume at temperature T :

$$V(T) = v_f(T) + w_f(T) \quad (2)$$

It is assumed also that the relaxation process is a direct and controlled function of free volume.

25 By cooling a poled polymer medium infinitely slow, a break in the volume-temperature curve is obtained at a temperature T_∞ . At this transition temperature, the

5

10

V

v

a

15

W.

T

20

T

25

p

$$\frac{dv(T,t)}{dt} = \frac{-w_f(T)}{\tau(w_f)} \quad (6)$$

This equation indicates that the rate of volume relaxation depends on:

- 5 (a) temperature;
- (b) departure from equilibrium free volume; and
- (c) size of free volume.

In accordance with the theoretical model as derived above, the initial fast decay of $X^{(2)}$ activity can be attributed
 10 to the relaxation of the largest free volumes. These free volumes are the furthest from the equilibrium, and therefore relax fastest as predicted by equation (6) above.

At the molecular level, for the free volume to change the polymer molecules must undergo a position adjustment.
 15 However, the rate at which the polymer molecules can adjust position is a sensitive function of free volume, and free volume itself is varying with time. Thus, after the initial fast decay of $X^{(2)}$ activity in a poled medium, the $X^{(2)}$ relaxation rate due to the remaining "bulk" free volume becomes
 20 a predictable parameter by the modified WLF equation.

The experimental time constants, obtained from least-square fits, for two of the side chain polymers described in the Example are as follows:

B'/butyl methacrylate (25/75) $t_{long} = 4.1E2$ min $T_g = 68^\circ C$

25 B'/butyl methacrylate (50/50) $t_{long} = 6.2E4$ min $T_g = 93^\circ C$ where
 B' is N-methyl-4-[2-(4-nitrophenyl)ethenyl]-
 phenylamino-2-ethyl-2-methyl-2-propenoate.

Brief Description of the Drawings

Fig. 1 is a graphical representation of the temperature versus time of the poling and quenching of a typical melted side chain polymer. As generally used herein, 5 quenched polymers are those which are cooled from T_g to room temperature in about thirty minutes.

Fig. 2 is a graphical representation of the temperature versus time of the poling, slow cooling, and annealing of a typical melted side chain polymer. Slow cooling 10 to the annealing temperature is generally carried out at a rate of from about 0.1 to about 0.5°C per minute in accordance with the present invention.

Fig. 3 through Fig. 6 are graphical representations, respectively, of the $X^{(2)}$ decay versus time of poled, quenched 15 and stored side chain polymers, and of poled, annealed and stored side chain polymers, as described in the Example.

The following Example is further illustrative of the present invention. The components and specific ingredients are presented as being typical, and various modifications can be 20 derived in view of the foregoing disclosure within the scope of the invention.

EXAMPLE

This Example illustrates process embodiments for the preparation of $X^{(2)}$ media with improved nonlinear optical 25 stability in accordance with the present invention.

Sample Preparation

Samples are prepared by spin coating a solvent solution of a nonlinear optically responsive side chain polymer



onto an ITO (indium-tin oxide) coated glass slide. The polymer layer is about 2-5 μm in thickness.

The ITO coating is an electrical conductor, and functions as one of the two electrodes required for molecular orientation of the polymer with an electric field. The second electrode is provided by the thermal evaporation of gold on the upper surface of the polymer layer. Lead wires are attached to the two electrodes.

Poling

10 A Mettler* Heating Stage FP800 is used to control the temperature of the poling sample. The FP800 is programmed to control temperature ramp rates and annealing times. The poling field is generated with a Kepco* OPS 3500 DC Power supply. A voltage of about 100 V/ μm is applied to the sample.

15 $\chi^{(2)}$ Measurement

A sample is poled with the applied field, and a second harmonic intensity level is determined as a means of monitoring the degree of orientation alignment of the nonlinear optically responsive side chains of the polymer molecules. The second harmonic intensity level is determined by directing an incident laser beam of 1.34 μm perpendicular to a sample surface, and then transmitted radiation at twice the frequency (670 μm) is measured at the other side of the sample.

The output second harmonic intensity from the polymer layer is a function of its second order nonlinear susceptibility $\chi^{(2)}$ which in turn is a function of the degree of alignment of the polymer side chains, i.e. of the degree of

*Trade-mark



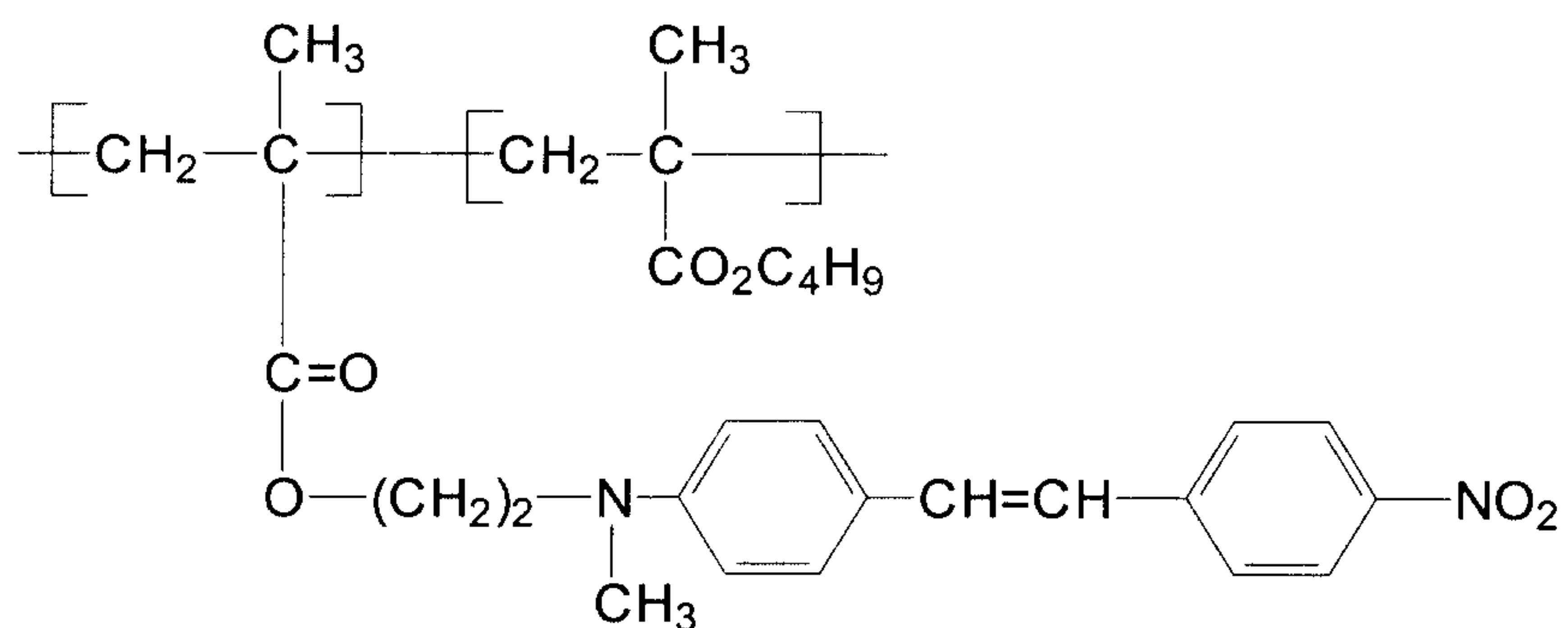
macroscopic noncentrosymmetry in the polymer layer. A completely random molecular orientation is centrosymmetric and nominally the second harmonic output is zero.

Nonlinear Optical Stability

- 5 The nonlinear optical stability of a poled sample is determined by monitoring the second harmonic output at the initial poling stage, and then at periodic time intervals during the cooling cycle under the electric field, and during the subsequent storage period at a given temperature.
- 10 The normalized $X^{(2)}$ relaxation curves for several side chain copolymers are determined. FIG. 3, FIG. 4, FIG. 5, and FIG. 6 represent plots of $X^{(2)}$ relaxation curves for polymers which are quenched after poling, or which are annealed after poling, while still subjected to the electric field effect.
- 15 The storage temperature cycle is without the electric field effect to permit observation of nonlinear optical activity loss.

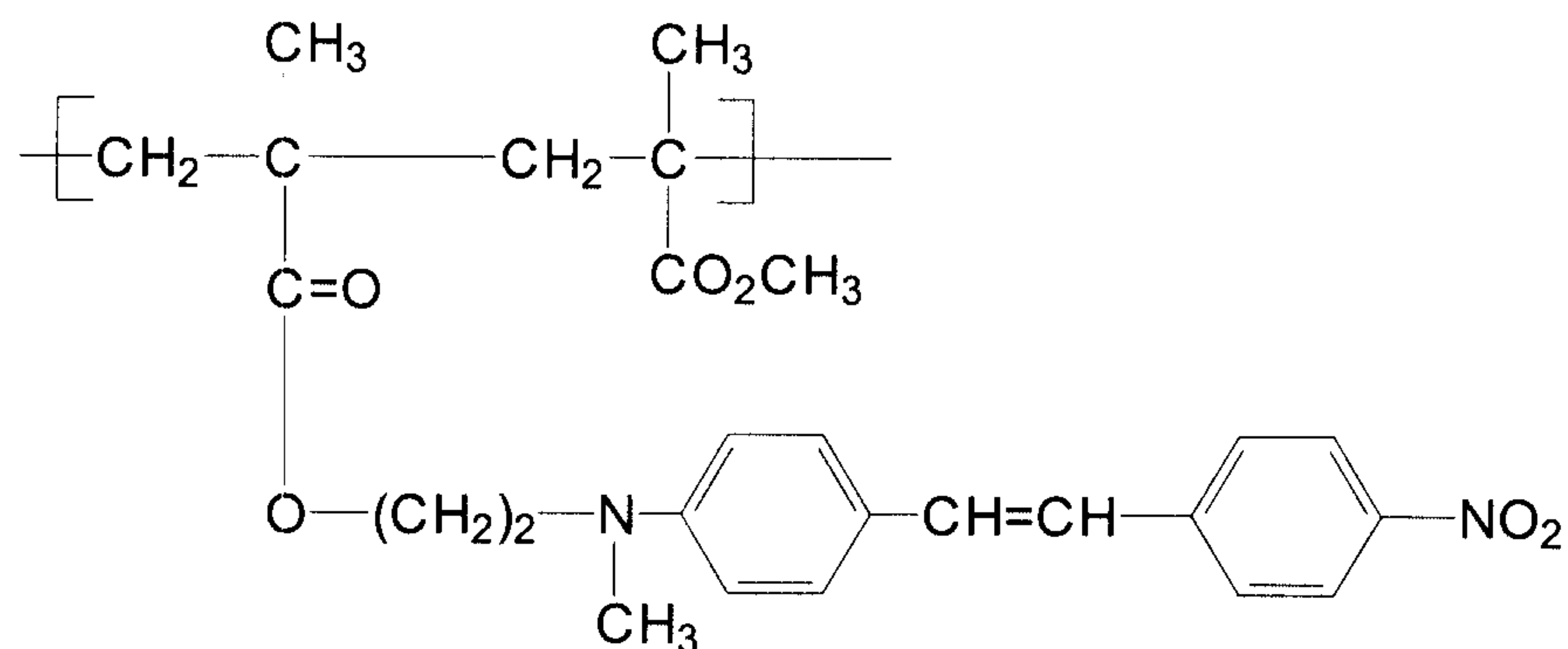
The B'/butyl methacrylate 50/50 copolymer I represented in FIG. 3 has a glass transition temperature (T_g) of 93°C, and corresponds to the formula:

5



The B'/methyl methacrylate 50/50 copolymer IV as represented in FIG. 6 has a glass transition temperature (T_g) of 135°C, and corresponds to the formula:

5



10

The figures demonstrate that a noncentrosymmetric side chain polymer medium has improved nonlinear optical stability if after poling and while maintaining the electric field effect the oriented polymer medium is annealed over a time period sufficient to achieve a thermal relaxation equilibrium in the oriented polymer medium.

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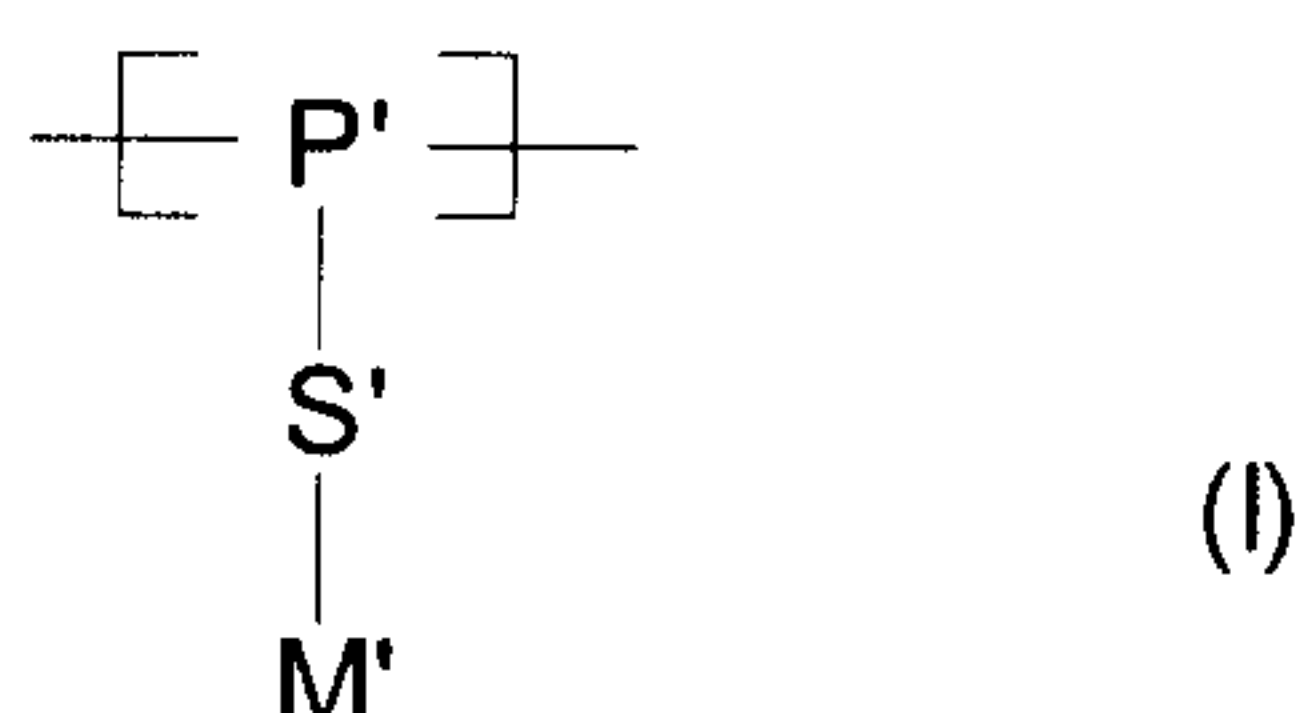
WHAT IS CLAIMED IS:

1. A process for producing a second order nonlinear optical medium having a stable noncentrosymmetric orientation of polymer molecules, which process comprises
(1) heating a film of a polymer with pendant side chains to a temperature of at least about the polymer glass transition temperature(T_g); (2) subjecting the polymer medium to an external electric field to induce noncentrosymmetry in the polymer medium by molecular orientation of the polymer side chains which exhibit second order nonlinear optical susceptibility; and (3) cooling the noncentrosymmetric polymer medium to a temperature between about T_g and 20°C to solidify the polymer medium while maintaining the electric field effect and the polymer molecular orientation, wherein the temperature cycle between T_g and 20°C is over a period of time sufficient to achieve ordered thermal relaxation and stabilization of the induced second order properties in the oriented polymer medium.

2. A process in accordance with claim 1 wherein the temperature cycle in step(3) is over a period between about thirty minutes and 300 hours.

3. A process in accordance with claim 1 wherein the glass transition temperature of the polymer is in the range between about 60°C - 250°C .

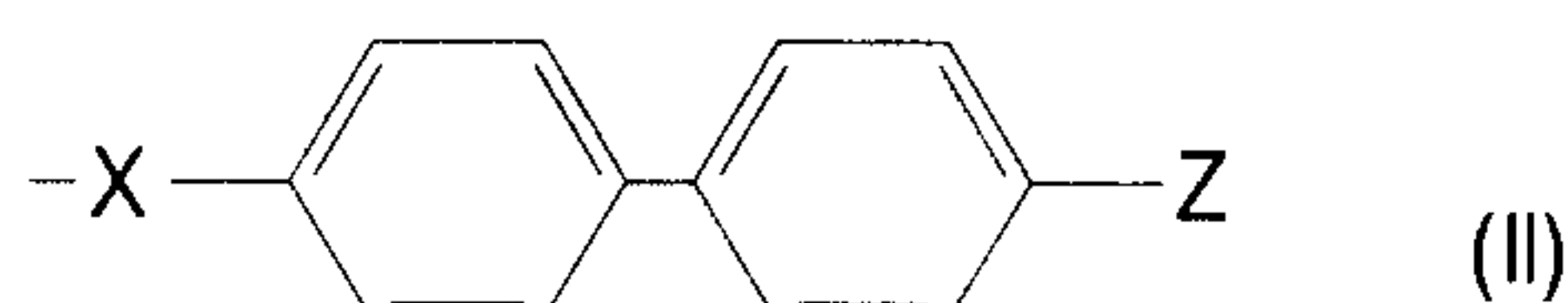
4. A process in accordance with claim 1 wherein the polymer is characterized by a recurring monomeric unit corresponding to the formula:

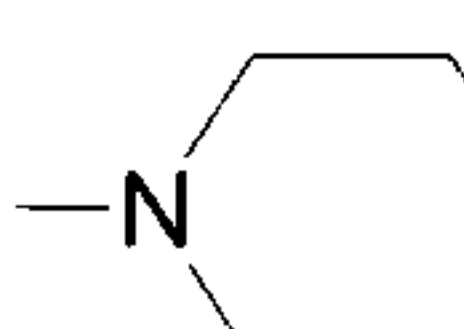
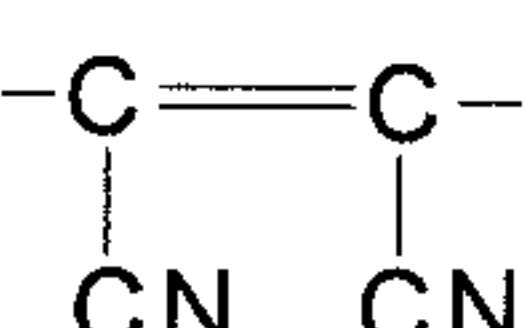


where P' is a polymer main chain unit, S' is a side chain flexible spacer group having a linear chain length of about 1-20 atoms, M' is a side chain pendant group which exhibits second order nonlinear optical susceptibility, and where the recurring monomeric unit comprises at least 20 weight percent of the polymer, and the polymer has a glass transition temperature above about 60°C.

5. A process in accordance with claim 4 wherein the pendant M' group in the polymer side chain contains a biphenyl structure.

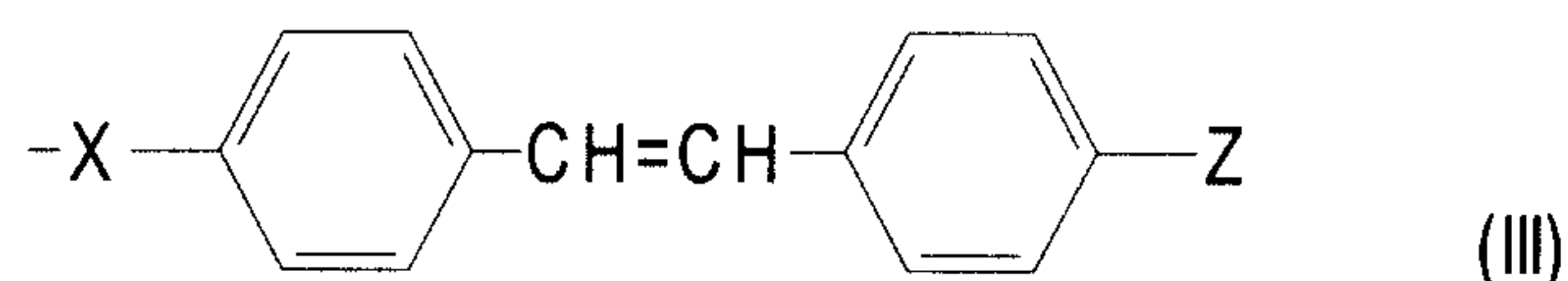
6. A process in accordance with claim 4 wherein the pendant M' group in the polymer side chain has the following structure:



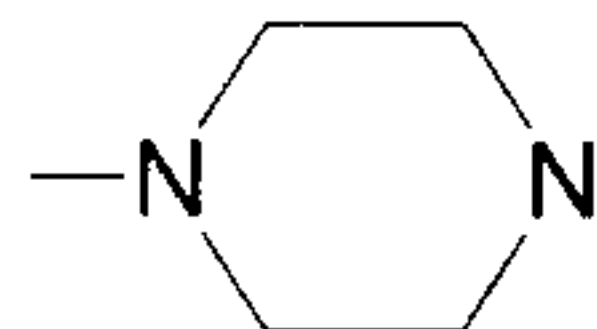
where X is -O-, -S-, -NR-,  or ; R is hydrogen or a C₁-C₄ alkyl substituent; and Z is -NO₂, -CN, -CF₃, -SO₃CF₃, -CH=C(CN)-CN or .

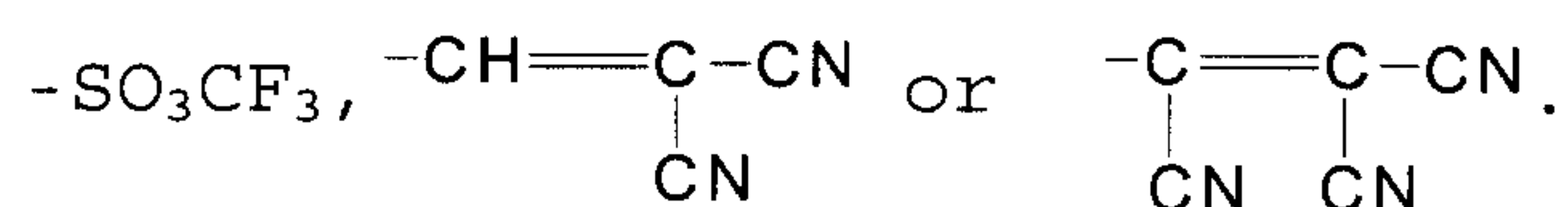
7. A process in accordance with claim 4 wherein the pendant M' group in the polymer side chain contains a stilbene structure.

8. A process in accordance with claim 4 wherein the pendant M' group in the polymer side chain has the following structure:



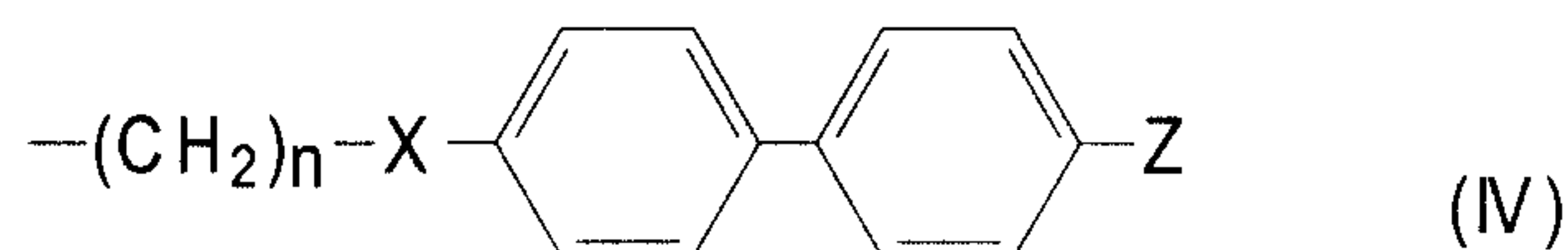
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where X is -O-, -S-, -NR-,  or ; R is hydrogen or a C₁-C₄ alkyl substituent; and Z is -NO₂, -CN, -CF₃,

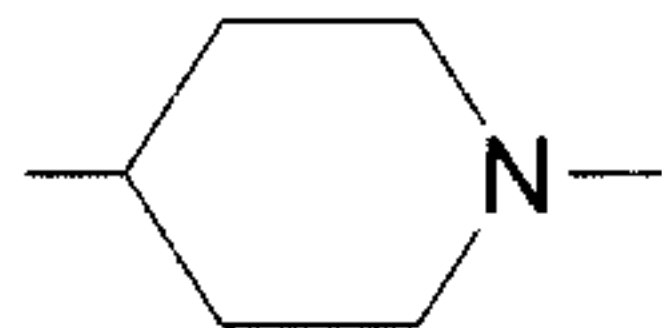
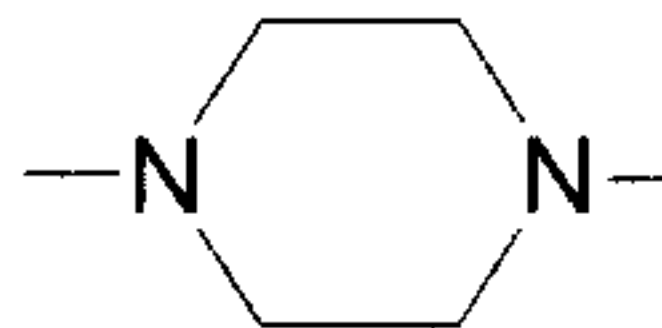


9. A process in accordance with claim 4 wherein the S' spacer group is -(CH₂)_n-, where n is an integer between about 2-12.

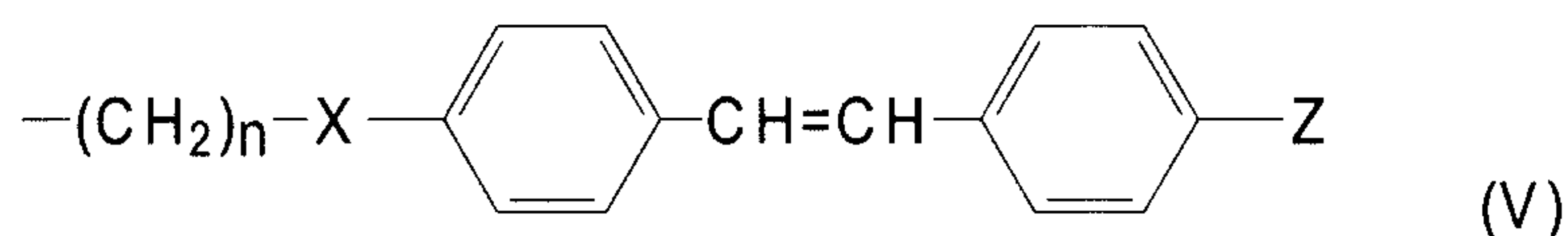
10. A process in accordance with claim 4 wherein the polymer side chains contain the following structure:



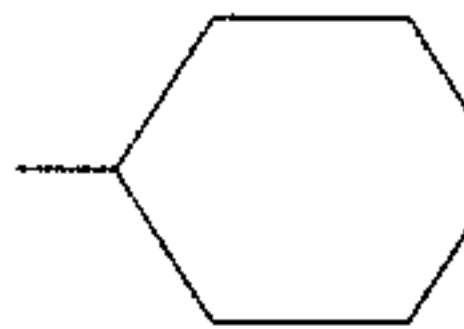
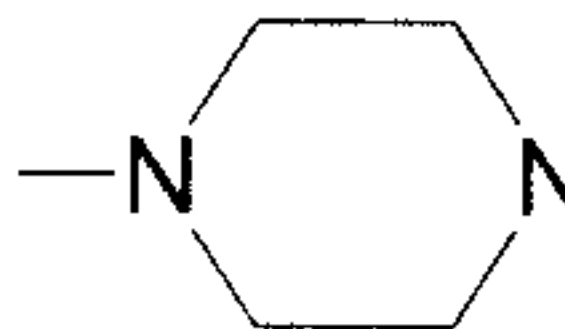
where n is an integer between about 2-12, X is -O-, -S-, -NR-,

 or ; R is hydrogen or a C₁-C₄ alkyl substituent; and Z is -NO₂, -CN, -CF₃, -SO₃CF₃, -CH=C(CN)-CN or -C(CN)=C(CN)-CN .

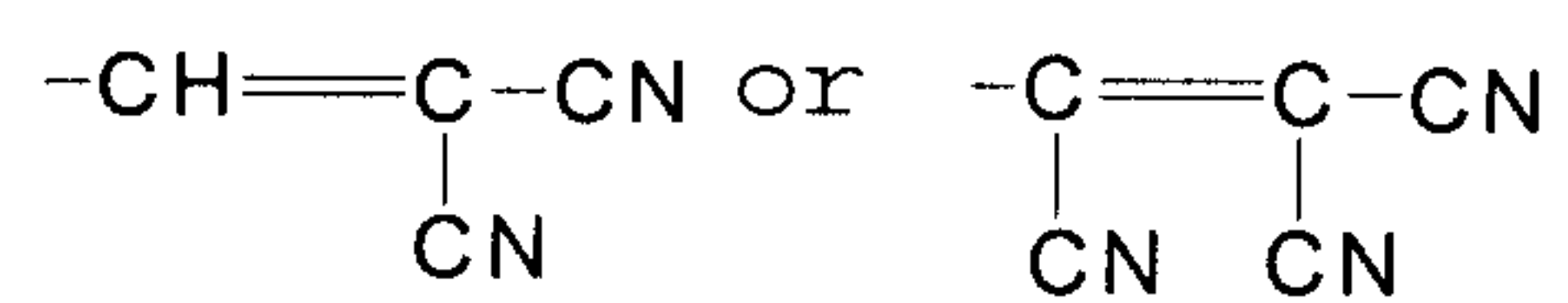
11. A process in accordance with claim 4 wherein the polymer side chains contain the following structure:



where n is an integer between about 2-12, X is -O-, -S-, -NR-,

 or ; R is hydrogen or a C₁-C₄ alkyl

substituent; and Z is -NO₂, -CN, -CF₃, -SO₃CF₃,



12. A process in accordance with claim 4 wherein the polymer main chain is a polyvinyl structure.

13. A process in accordance with claim 4 wherein the polymer main chain is a polysiloxane structure.

14. A process in accordance with claim 4 wherein the polymer main chain is a polyoxyalkylene structure.

15. A process in accordance with claim 4 wherein the polymer main chain is a polyamide structure.

16. A process in accordance with claim 4 wherein the polymer main chain is a polyester structure.

17. A process for producing a second order nonlinear optical medium having a stable noncentrosymmetric molecular orientation of polymer molecules, which process comprises (1) heating a film of a polymer with pendant side chains to a temperature in the range between about the polymer glass transition temperature(T_g) and 30°C; (2) subjecting the heated polymer medium to an external electric field to induce noncentrosymmetry in the polymer medium by molecular orientation of the polymer side chains which exhibit second order nonlinear optical susceptibility; and (3) maintaining the

noncentrosymmetric polymer medium in solid form in the temperature range between about T_g and 30°C while maintaining the electric field effect and the polymer molecular orientation, wherein the temperature cycle between T_g and 30°C is over a period of time between about thirty minutes and 300 hours sufficient to allow ordered thermal relaxation so as to stabilize the induced second order properties in the oriented polymer medium.

18. A process in accordance with claim 17 wherein the heating of the polymer medium in the process steps is at a temperature in the range between T_g and $0.5 T_g$ ($^\circ\text{C}$).

19. A process in accordance with claim 17 wherein the temperature cycle in step (3) is over a period between about 0.5-60 hours.

20. A process in accordance with claim 17 wherein the polymer film has a thickness between about 0.1-1000 microns.

21. A process in accordance with claim 17 wherein the external field is applied to the polymer film with a pair of electrodes having an applied voltage between about 10-1000 V/ μm .

22. A process in accordance with claim 17 wherein the polymer is a polyacrylate or polymethacrylate polymer or copolymer which has pendant side chains which exhibit second order nonlinear optical susceptibility, and the pendant side chains contain a biphenyl or stilbene structure.

23. A second order nonlinear optical medium comprising a stable noncentrosymmetric orientation of polymer molecules, wherein the polymer has side chains which exhibit second order nonlinear optical susceptibility, and wherein there is less than about 10 percent loss of second order nonlinear optical activity exhibited by the medium when the medium is maintained at 50°C for one year.

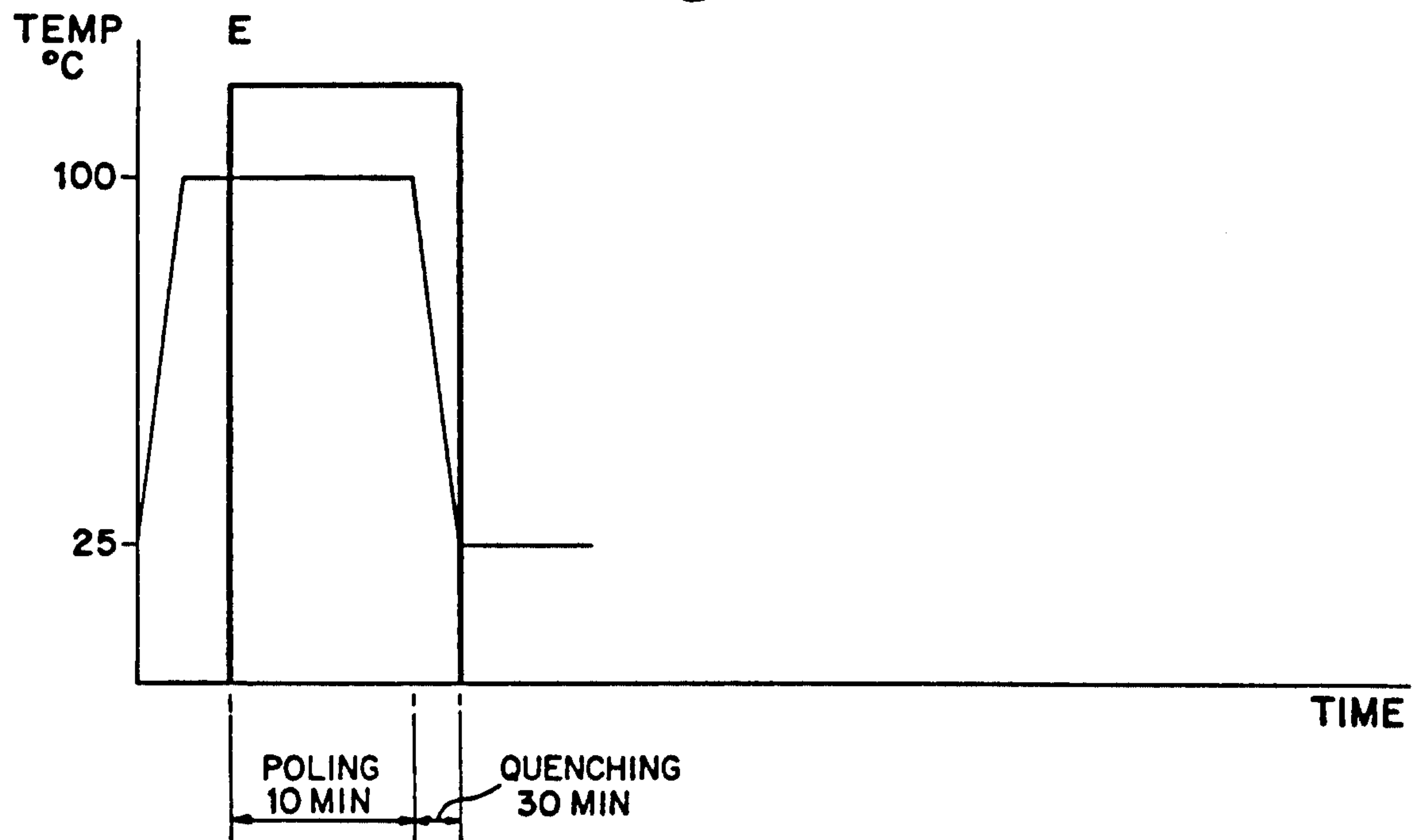
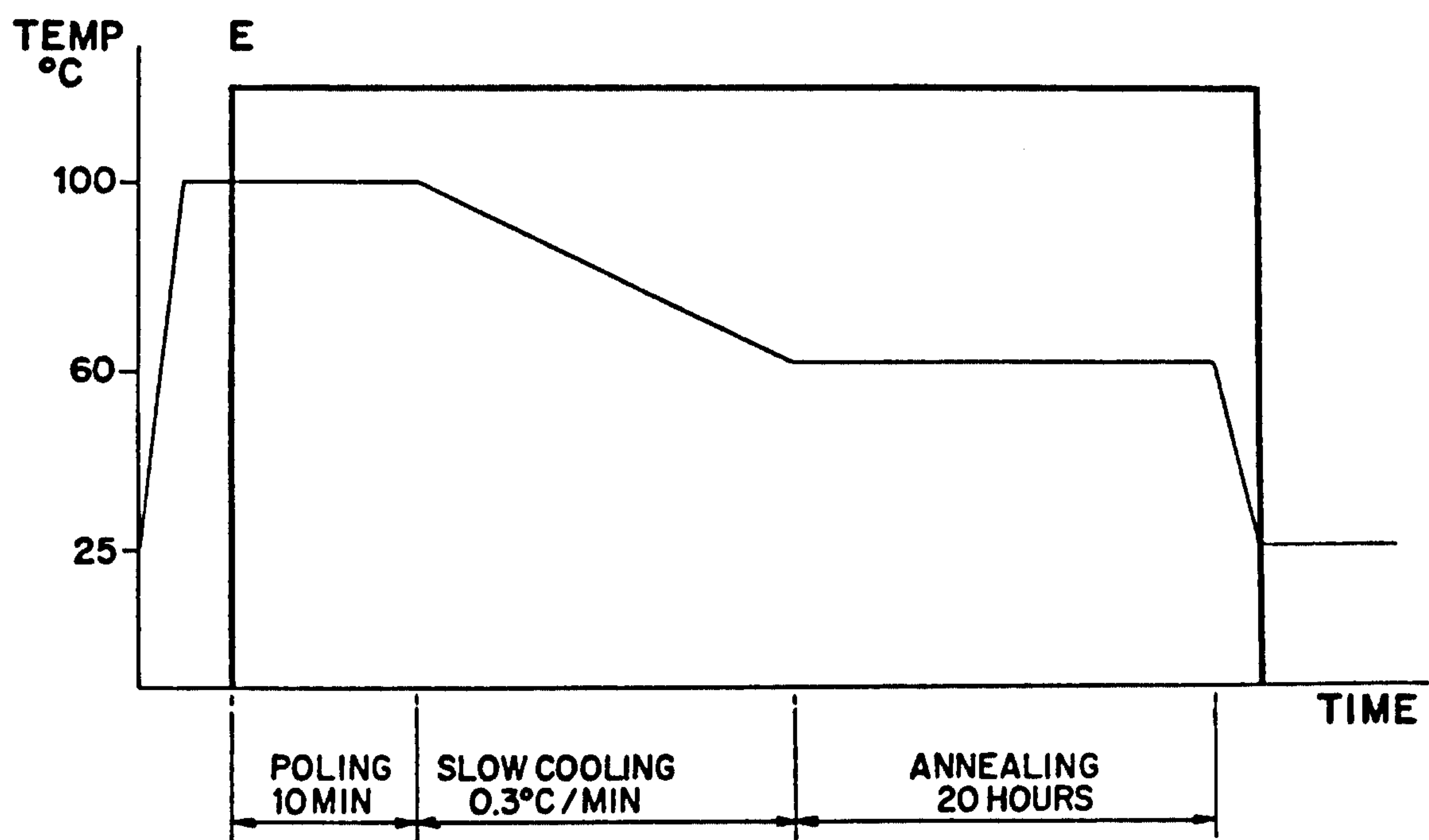
24. An optical light switch or light modulator device with a polymeric second order nonlinear optical component comprising a noncentrosymmetric medium of oriented polymer molecules, wherein the polymer has side chains which exhibit second order nonlinear optical susceptibility, and wherein there is less than about 10 percent loss of second order nonlinear optical activity exhibited by the optical medium when the medium is maintained at 50°C for one year.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS

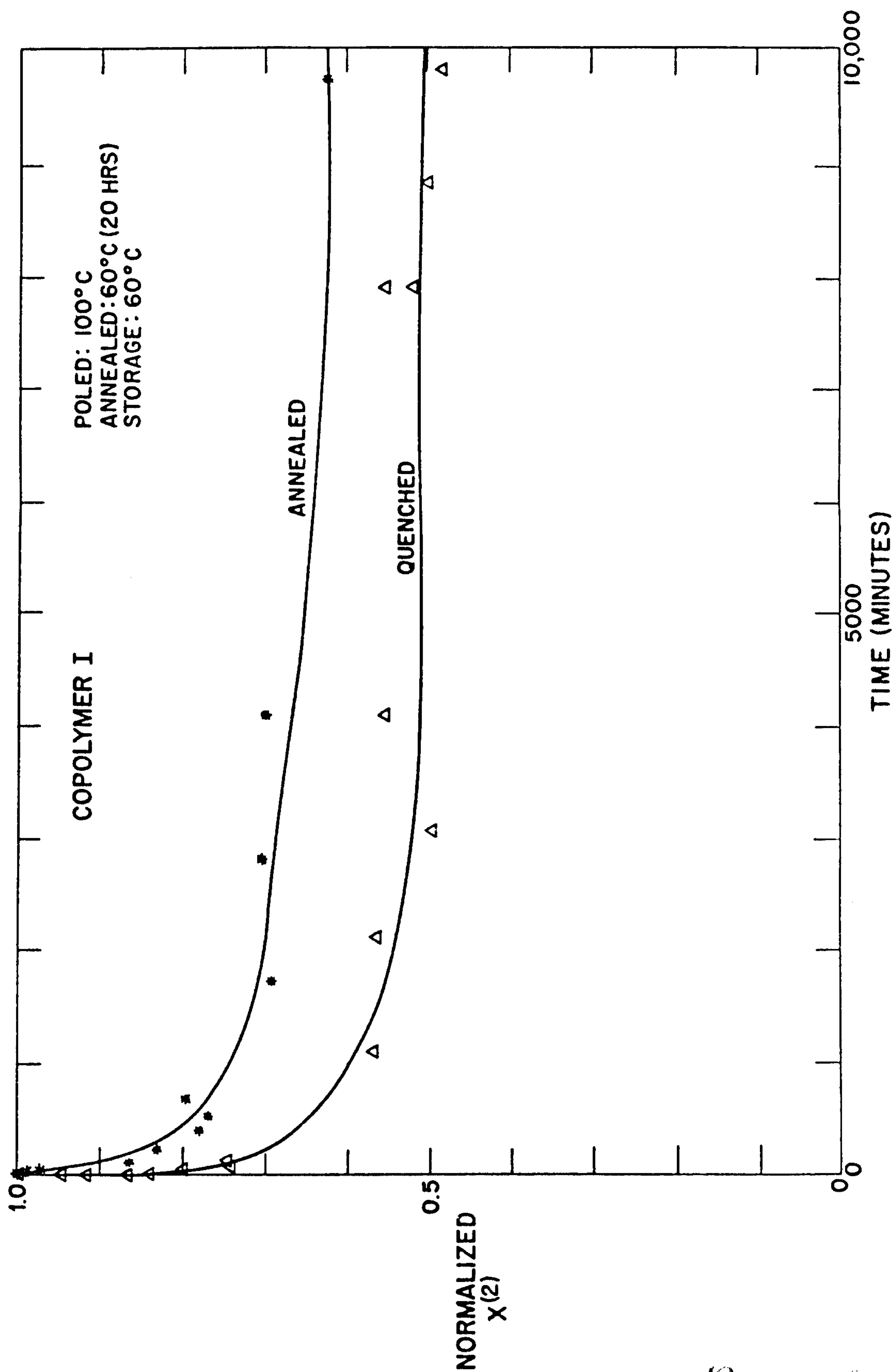


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Fig.1**Fig.2**

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Fig. 3



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Fig.4

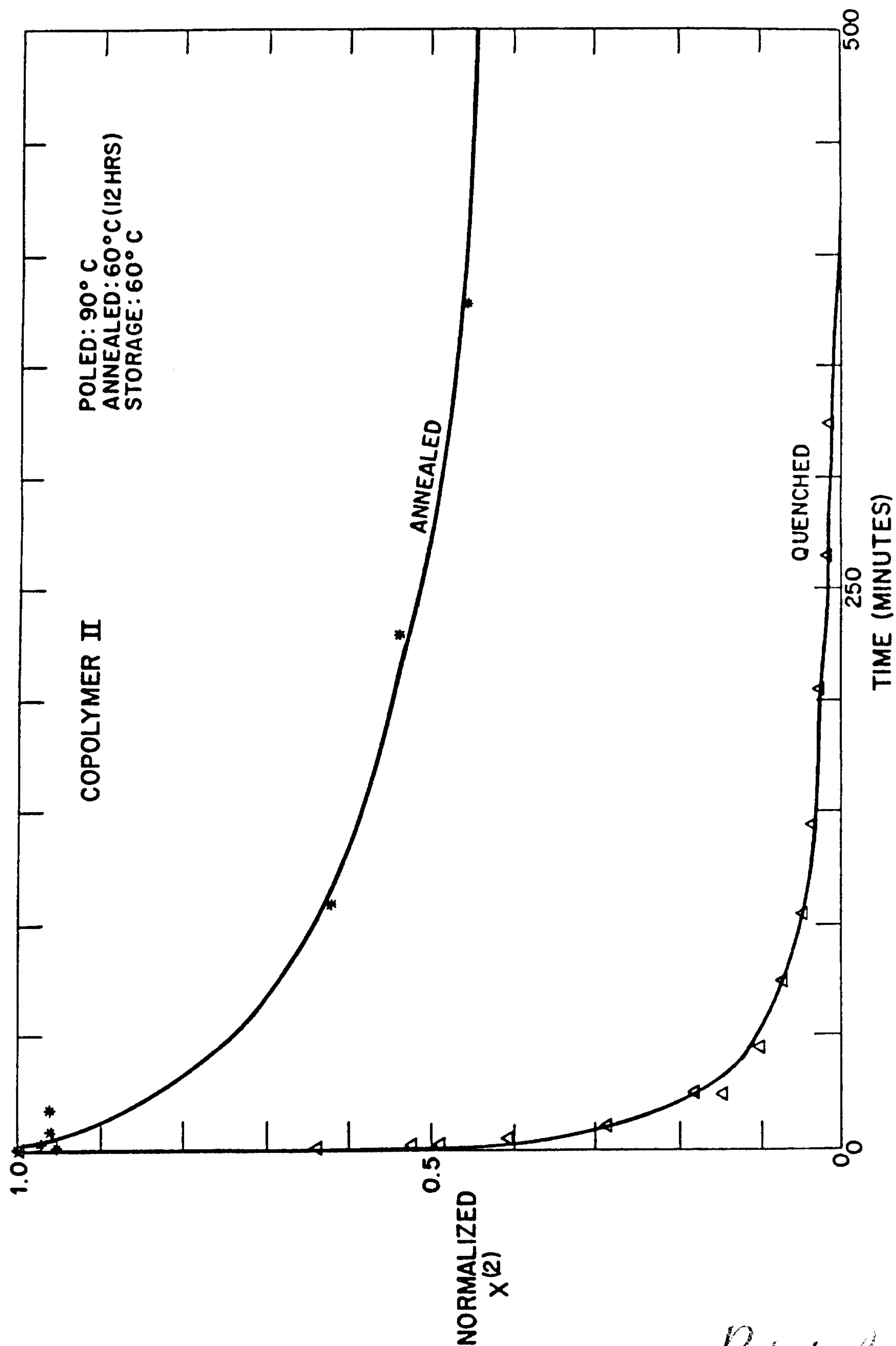
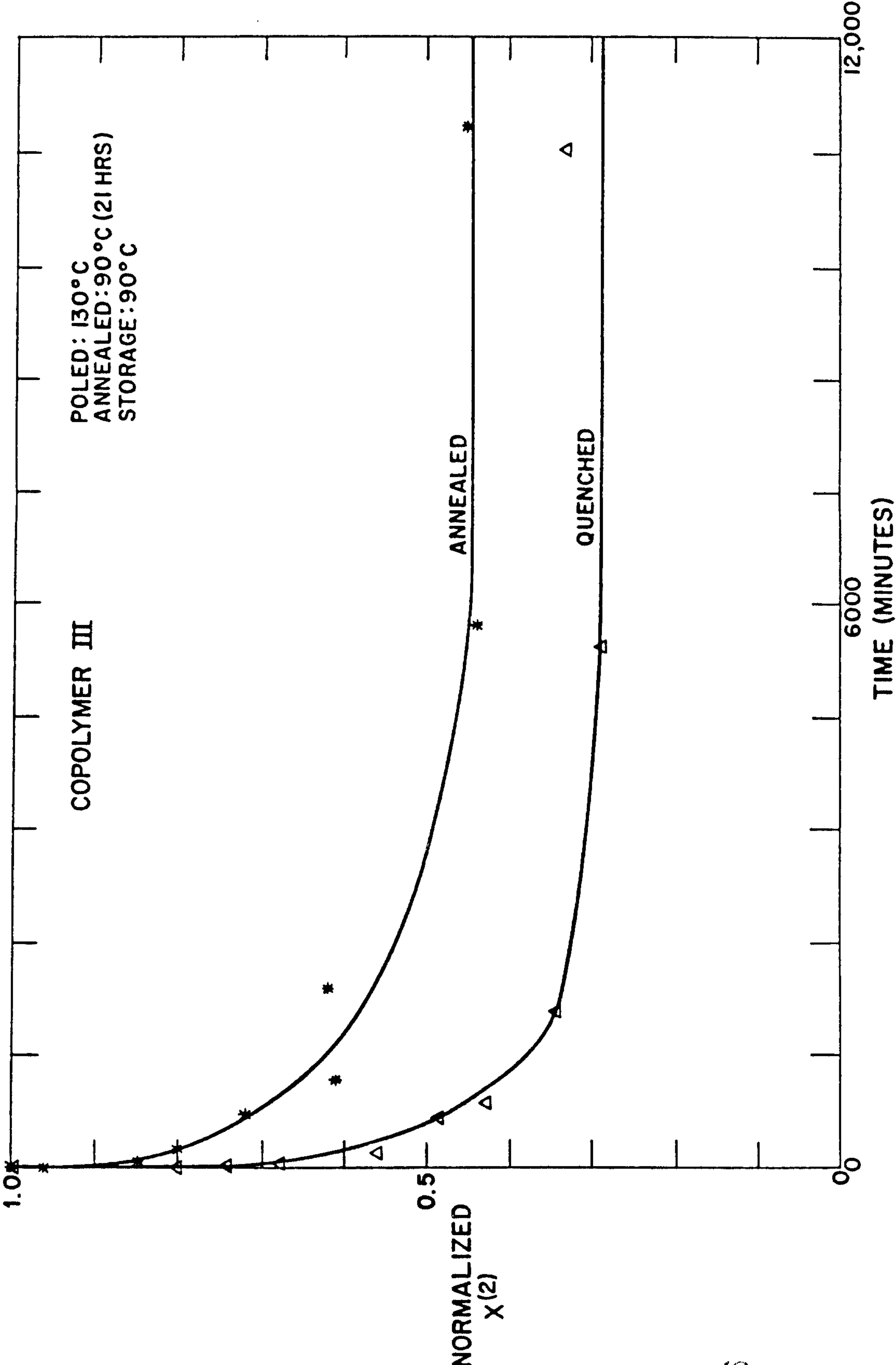


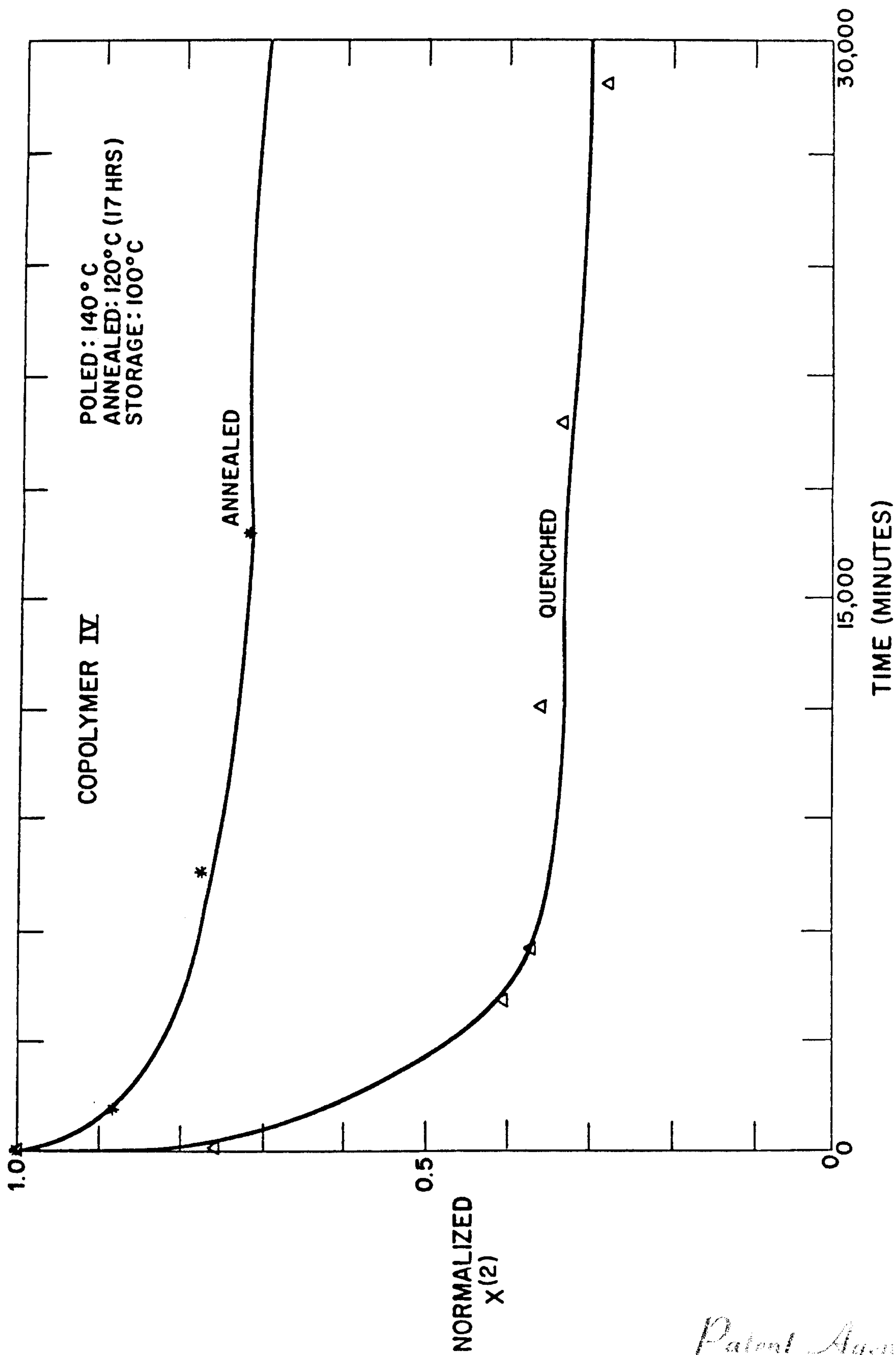
Fig. 5



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Fig. 6



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