

Diacetylene-Containing Polymers VII.[†] Synthesis and Characterization of New Diacetylene-Containing Polyesters and Copolyesters Derived from Dipropargyl-1,10-decanate, Dipropargyl Terephthalate, 4,4'-Dipropargyloxy Diphenyl, and 4,4'-Bis[(5-carbopropargyloxy)pentoxy]diphenyl

Sergei FOMINE, Simon SANCHEZ, and Takeshi OGAWA^{††}

*Instituto de Investigaciones en Materiales, Circuito Exterior,
Ciudad Universitaria, México DF 04510, Mexico*

(Received August 22, 1994)

ABSTRACT: A series of new thermoplastic diacetylene containing polyesters and copolyesters was synthesized and characterized. The copolyesters had melting points as low as 50°C and were topochemically cross-linkable on electron beam irradiation. One of the copolymers was found to form a nematic melt in the region of 48—67°C and was cross-polymerizable in the liquid-crystalline state to form a polydiacetylene network. The tensile strength and Young's moduli of the polymers reached as high as 145 MPa (1 Mrad) and 535 MPa (5 Mrad) respectively. The values decreased with decrease in degree of crystallinity or melting point of the crystallites and the tensile strength went through a maximum on irradiation with an electron beam. Electron beam irradiation brought about a decrease in elongation at the break and increase in Young's modulus.

KEY WORDS Polydiacetylene / Polyester / Mechanical Properties / Liquid Crystals /

Polydiacetylenes (PDAs) have attracted considerable attention as candidates for materials for nonlinear optical (NLO) applications.¹ For use in optical devices, PDA must be processed into desired forms such as thin films of satisfactory optical quality. The current interest in PDAs appears to be focused on processing of diacetylenic materials. One of the methods to obtain PDA-containing films is to synthesize diacetylene(DA)-containing polymers which are then made into thin films and DA groups in the films are cross-polymerized to develop PDA networks in the film.²

However, only a few works have been reported on the development of DA-containing engineering plastics. The reason for this is that DA-containing polymers of high molecular

weight have not been obtained in the past, probably due to inadequate polymerization conditions used.

The synthesis of a polyimide from benzene-tetracarboxylic dianhydride and 4,4'-diaminodiphenylbutadiyne is described in a patent,³ but the polymer appears to be quite intractable. Kato *et al.*⁴ studied the polymerization of a series of hexa-2,4-diynylene diacrylamide, and DA-containing oligomeric fumarate and fumaramide. Materials of high modulus and hardness were obtained, but possible applications are not mentioned. Rubner⁵ obtained fibers spun from poly(hexamethylene-10,12-docosadiyne-1,22-diamide) prepared by the interfacial polycondensation of hexamethylenediamine and 10,12-docosadiyne-1,22-diacid

[†] Part VI. S. Fomin, A. Maciel, and T. Ogawa, *Polym. J.*, **26**, 1270 (1994).

^{††} Author for correspondence.

chloride. The ultimate tensile strength of the fiber increased by 100% when irradiated by an electron beam with a dose of 80 Mrad.

The present authors synthesized high molecular weight DA-containing aliphatic polyesters by the oxidative coupling polymerization of bisacetylenic diesters,⁶ and studied their mechanical properties.⁷ The cast films of poly(octa-3,5-diynylene sebacate) for example, had a tensile strength of 250 MPa and Young's modulus of 1.1 GPa, and the tensile strength increased to 330 MPa on irradiation with an electron beam with a dose of 0.2 Mrad and the Young's modulus increased to 1.63 GPa with a dose of 15 Mrad.

It must be borne in mind that DA-containing polymers may explode when overheated. When the above mentioned poly(octa-3,5-diynylene sebacate) was melted and pressed to extrude fibers, an explosion took place, probably due to the highly exothermic nature of thermal and pressure induced polymerization of DA groups.

From the point of view of processing, therefore, it is important to decrease the melting points of the polymers. It is well known that copolymerization decreases the melting point and crystallinity of polymers, and therefore copolymerization of different bisacetylenic diesters was carried out. The thermal and mechanical properties of the copolymers were investigated, and the results are reported in this paper.

EXPERIMENTAL

Materials

1,2-Dichlorobenzene (ODCB) was distilled in vacuum. *N,N,N',N'*-tetramethylenediamine (TMDA) was distilled before use. Other reagents were used as received (Aldrich).

Monomer Synthesis

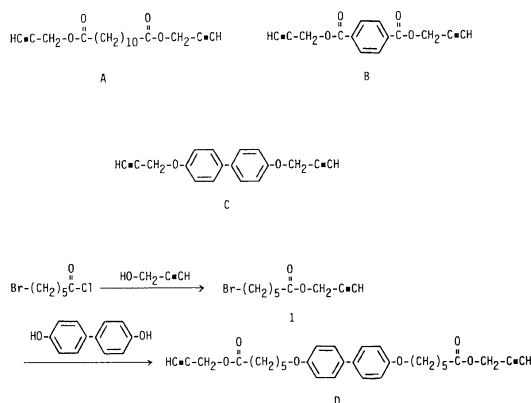
Dipropargyl 1,10-decanate (**A**) was prepared from propargyl alcohol and 1,10-decanedicarboxylic acid as follows; 30 g of 1,10-

decanedicarboxylic acid, 50 ml of oxalyl chloride and 50 ml of CH_2Cl_2 were refluxed overnight. The solvent and excess oxalyl chloride were rotoevaporated under vacuum and a 10% excess of propargyl alcohol dissolved in 100 ml pyridine was added while cooling at 0°C. The mixture was stirred for 3 hours at room temperature and poured into acidified water. The solid which precipitated was filtered off and purified by column chromatography (SiO_2 , benzene). Yield 79%, $T_m = 41^\circ\text{C}$, IR (cm^{-1}): 3280 (CC-H), 2120 ($\text{C}\equiv\text{CH}$), 1740 (C=O). ^1H NMR (in CDCl_3) 1.10–1.90 (m, 16H, $-(\text{CH}_2)_8-$), 2.10 (t, 4H, $-\text{COCH}_2-$), 2.20 (t, 2H, $\text{HC}\equiv\text{C}-$), 4.30 (d, 4H, $\equiv\text{C}-\text{CH}_2\text{OOC}-$). *Elemental analysis.* Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_4$: C, 70.55%; H, 8.55%, Found: C, 70.55%; H, 8.82%.

Dipropargyl terephthalate (**B**), and 4,4'-dipropargyloxy diphenyl (**C**) were prepared using methods adopted from the literature^{8,9} (for monomers **B** and **C**, respectively).

4,4'-Bis[(5-carbopropargyloxy)pentoxy]-diphenyl (**D**) was prepared in two steps from propargyl alcohol, 6-bromohexanoyl chloride and 4,4'-dihydroxydiphenyl as follows; to a solution containing 125 mmol of propargyl alcohol 9 ml of pyridine and 50 ml of benzene 125 mmol of 6-bromohexanoyl chloride were added dropwise at 5°C. After 2 hours stirring at room temperature the mixture was washed with dilute HCl and then with water and dried over MgSO_4 . Benzene was rotoevaporated and crude propargyl 6-bromohexanate (**1**) was obtained.

21.5 mmol of 4,4'-Dihydroxydiphenyl were dissolved in 70 ml dry *N*-methylpyrrolidone and to this solution were added 6 g anhydrous powdered K_2CO_3 and 60 mmol of propargyl 6-bromohexanate (**1**). The reaction mixture was stirred overnight at 90°C. The reaction solution was poured into water. The solid precipitated was washed with 2% KOH solution and then with water and crystallized 3 times from a hexane–benzene mixture. Yield 56%, $T_m = 78^\circ\text{C}$. IR (cm^{-1}): 3280 (CC-H),



Scheme 1.

2126 ($\text{C}\equiv\text{CH}$), 1740, 1760 ($\text{C}=\text{O}$). ^1H NMR (in CDCl_3) 1.10–2.00 (m, 12H, $-(\text{CH}_2)_3-$), 2.32 (t, 4H, $-\text{COCH}_2-$), 4.00 (t, 4H, $-\text{OCH}_2-$), 4.65 (d, 4H, $\equiv\text{C}-\text{CH}_2-\text{OOC}-$), 6.70–7.50 (m, 8H, arom.) *Elemental analysis.* Calcd for $\text{C}_{30}\text{H}_{34}\text{O}_6$: C, 73.44%; H, 6.99%. Found: C, 73.19%; H, 7.12%.

The structures of the monomers **A**, **B**, **C**, and the synthesis of monomer **D** are shown in Scheme 1.

Polymerization

2 g of a monomer or a mixture of the monomers, 0.09 g of CuCl , 1.8 ml of TMDA, and 15 ml of ODCB were heated to 75°C . Oxygen was bubbled through the reaction mixture with stirring for 30 min. The reaction mixture was poured into *n*-propanol, acidified with HCl and stirred for 5 hours. The precipitate was filtered off, washed with water and *n*-propanol and dried in vacuum at room temperature. All polymers had two peaks in the FT-IR spectra in the region of 2260 and 2160 cm^{-1} , indicating diacetylene group formation and absorption in the regions of 3280 and $2120\text{--}2130\text{ cm}^{-1}$, showing terminal acetylenic groups to have disappeared.

Measurements and Sample Preparation

The inherent viscosity of the copolymers was measured in 0.5% solution in CHCl_3 at

25°C . Molecular weight was determined by GPC using polystyrene standard in THF with a flow of 1 ml min^{-1} at 30°C with a Varian 9012. DSC and TMA were performed at heating rates of 20 and 5°C min^{-1} , respectively, under nitrogen flow with a Dupont 2100. IR-spectra were taken using a Nicolet 510p FT-IR spectrometer. ^1H NMR spectra were taken in CDCl_3 solution using a Jeol PMX60SI spectrometer. UV-spectra were taken using a UV-260 Shimadzu. Liquid crystalline state formation was observed using an Olympus B071 polarizing microscope equipped with a hot stage. X-Ray diffractometry was performed using a Siemens D-500 diffractometer with Cu-K_α radiation of 1.540 Å.

The samples for mechanical testing were prepared as follows: The purified polymers were heated above their melting points and then pressed into sheets of about 0.1 mm thickness during 30 sec. Strips $17 \times 5 \times 0.1\text{ mm}$ were cut from the polymer sheets and oriented by stretching by 200% at room temperature using an Instron 1125 with a crosshead speed of 5 mm min^{-1} . Irradiation of the oriented samples was carried out with electron beam irradiation in air. Mechanical testing of the oriented samples was carried out with an Instron 1125 at a crosshead speed of 5 mm min^{-1} at room temperature, using the Instron series IX automated materials testing system, version 5. Each value given in the mechanical testing data is mean value for five samples.

RESULTS AND DISCUSSION

As seen from Table I, the polymers and copolymers soluble in reaction media had high molecular weights. Those containing much rigid monomer, such as A40B60, A20B80, B100, A60C40, and A40C60, which precipitated during the polymerization, and had lower molecular weights. However, some were still soluble in chloroform and gave films on solution casting. The homopolymer, D100, has

Table I. Some physico-chemical properties of DA-containing polymers

Polymers	Composition/mol %				T_g^a	T_m^b	T_i^c	η_{inh}^d	Degree of crystallinity	Mol wt. M_w
	A	B	C	D	°C	°C	°C	dl g ⁻¹	%	
A100	100	0	0	0	0	84	—	1.3	63	73000
A80B20	80	20	0	0	0	77	—	1.2	50	72000
A60B40	60	40	0	0	3	52	—	1.2	44	71000
A40B60	40	60	0	0	0	48	67	0.5	38	28000
A20B80	20	80	0	0	-5	102	—	—	58	—
B100	0	100	0	0	0	—	—	—	68	—
A80C20	0	80	20	0	-3	73	—	1.1	11	70500
A60C40	0	60	40	0	-5	62*	—	0.4	12	18000
A40C60	0	40	60	0	—	—	—	—	71	—
D100	0	0	0	100	—	131	—	0.6	12	32000
A50D50	50	0	0	50	—	90	—	0.6	9	33500

^a Glass transition temperature. ^b Melting transition. ^c Isotropization. ^d Inherent viscosity.

already been prepared by Durlikov *et al.*⁸ They used dimethylformamide (DMF) as a polymerization solvent and reported that the polymer was soluble in DMF. D100 in this work was prepared at 75°C in ODCB and was insoluble in all solvents except concentrated sulfuric acid, when the polymerization was continued until the polymer precipitated *e.g.*, 5–10 minutes after starting.

The results of the characterization of the polymers are also presented in Table I. All are semicrystalline and the crystallinity and melting transition temperatures go through a minimum on changing the composition of the copolymers for copolymers of **A** and **B** monomers, reaching about 50°C and 40% respectively for copolymers A60B40 and A40B60. This behavior of the copolymers proves their random structures.

The copolymers of monomers **A** and **C** had lower crystallinity than the copolymers of **A** and **B**. This is probably because the more rigid comonomer **C** hindered crystallization of the copolymer. Similar to the copolymers of **A** and **B** described above, in the copolymerization of monomers **A** and **C** at first there was a reduction in the melting transition temperature of the copolymers but on increasing the content of the rigid component above

40 mol%, infusible and insoluble copolymers were formed. Copolymer A40C60 had a rather high crystallinity of 71% which may be due to the low molecular weight of the latter (the copolymer precipitated during the first several minutes of polycondensation).

Monomer **D** was found to have liquid crystalline properties: its DSC curve had three endotherms on heating (Figure 1) at 78, 82.5, and 86.6°C. The first one was a crystal-mesophase transition, the second a transition from one mesophase to another and the third, isotropization. The first and the second mesophase showed typical conic nematic textures and there were no textural changes in the region of the second endotherm, indicating both mesophases to be nematic.

The DSC curve of homopolymer **D100** is shown in Figure 1. Unlike the monomer **D**, **D100** showed only one transition at 131°C corresponding to a melting transition according to X-ray data and optical observations.

The oxidative polycondensation leads to the formation of a rigid diacetylene structure which elevates the melting transition temperature for the polymer making the liquid crystalline state thermodynamically unstable and this may be the reason for the disappearance of the mesophase in **D100**.

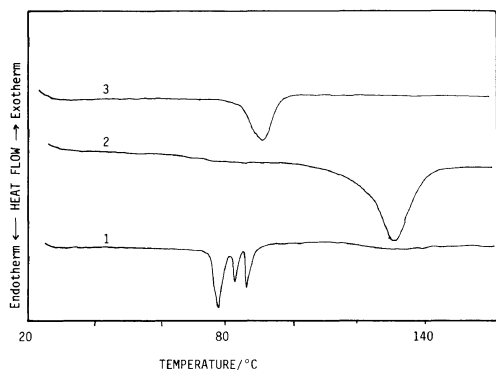


Figure 1. DSC curves of monomer **D** (1), polymers **D100** (2), and **A50D50** (3).

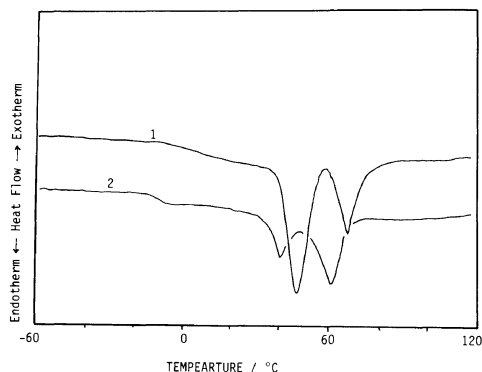


Figure 2. DSC curves of copolymers **A40B60** (1) and **A60C40** (2).

We reduced the melting transition temperature of **D100** by copolymerization with the flexible monomer **A**. As one can see from the copolymers of **A** and **B**, maximal reduction of the melting transition temperature was achieved when are about equimolar of each monomers copolymerized. The DSC curve of copolymer **A50D50** is shown in Figure 1. The melting transition temperature decreased to 90°C. However, just one endotherm was observed in this case.

The DSC curves of copolymers **A40B60** and **A60C40** are shown in Figure 2. These two copolymers had two endotherms in their DSC curves, suggesting mesophase formation. In the case of **A60B40** in the region between endotherms, typical conic nematic textures were observed, indicating nematic phase formation. In the case of **A60C40** birefringence was observed in the region between two endotherms; however, no definitive liquid crystalline textures were seen. To distinguish between crystal-crystal and crystal-mesophase transition TMA analysis of copolymers **A40B60** and **A60C40** was performed (Figure 3). In the case of **A40B60**, the copolymer starts to flow at the temperature of the first endotherm thus confirming the mesophase formation. In the case of **A60C40** the copolymer starts to flow at the temperature of the second endotherm indicative of crystal-

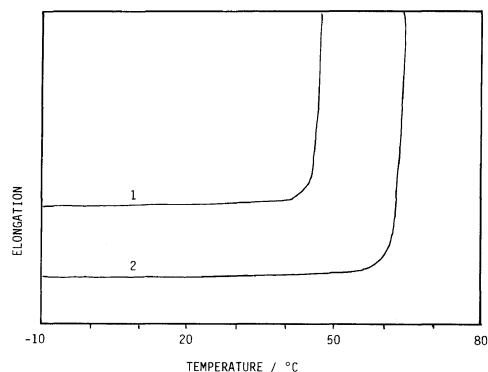


Figure 3. TMA curves of copolymers **A40B60** (1) and **A60C40** (2).

crystal transition in **A60C40**, unlike **A40B60**.

The cross-polymerization of **A40B60** on electron beam irradiation was carried out in solid, liquid crystalline and liquid states. Figures 4 and 5 show the FT-IR and UV-visible absorption spectra of **A60C40**, respectively, after irradiation at 20°C (solid state), 60°C (liquid crystalline state), and 100°C (liquid state) with an electron beam (50 Mrad). As can be seen from Figure 5, samples irradiated at 20 and 60°C showed absorption maxima at about 500 nm whereas the sample irradiated at 100°C showed only a tail in the visible region. However, the FT-IR-spectra of all three samples are similar to one another (Figure 4). All three samples on irradiation developed an

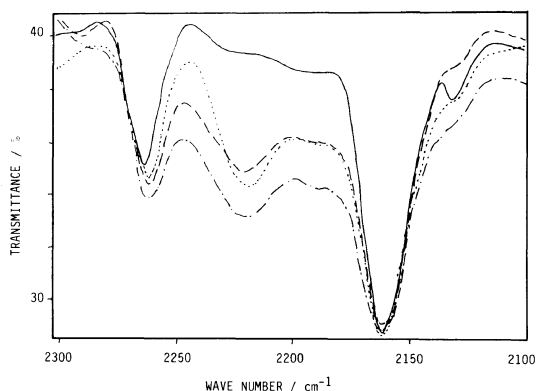


Figure 4. FT-IR spectra of copolymer A40B60; unirradiated (—), irradiated at 20°C (---), irradiated at 60°C (-·-·-·), irradiated at 100°C (····) (50 Mrad).

absorption bands at 2220 cm^{-1} characteristic of conjugated triple bonds of polydiacetylenes.⁶ This means that in the solid, liquid crystalline and liquid states, cross-polymerization takes place with polydiacetylene network formation with long polydiacetylene sequences. In the liquid state, however, shorter polydiacetylene sequences are formed as can be seen from UV-visible spectra, probably because of the enhanced mobility of the polymer chains in the liquid state. The spectra are typical of those of amorphous polydiacetylenes, although some diacetylenes undergo 1,4-polyaddition in the liquid crystalline state to form polydiacetylenes.¹⁰ The cross-polymerization of diacetylene-containing polymers in the liquid crystalline state with polydiacetylene network formation, has not been reported previously. It was found in this work that topochemical polymerization takes place also in the liquid crystalline state.

The mechanical properties of the copolymers and their dependence on electron beam irradiation are presented in Table II. To compare the mechanical properties of the copolymers, only those copolymers with about equal molecular weights were chosen. As can be seen from Table II elongation at the break, tensile strength and Young's modulus of unirradiated polymers depend on the degree of

Table II. Mechanical properties of DA-containing polymers

Sample	Dose	Strain at break	Tensile strength	Initial Young's modulus
	Mrad	%	MPa	MPa
A100	0	54	138	483
A100	1	38	145	480
A100	5	14	82	535
A80B20	0	111	100	206
A80B20	1	72	106	254
A80B20	5	28	34	303
A60B40	0	66	27	153
A60B40	1	60	29	162
A60B40	5	42	11	185
A80C20	0	130	41	115
A80C20	1	119	44	123
A80C20	5	52	51	182

crystallinity and melting point of crystallites, because measurements were carried out at the temperature higher than T_g of the copolymers.

The tensile strength and Young's modulus of unirradiated copolymers decreased with decrease in the melting points of the crystallites in the copolymers of monomers **A** and **B** because lowering of the melting transition temperature means reduction of the interactions between macromolecules in the crystallites. Thus, polymers A80B20 and A80C20 have almost equal melting transition temperatures (77 and 73°C, respectively). However, their crystallinity differ greatly, (50 and 11%, respectively) as shown by their different tensile strengths. The first copolymer had a tensile strength more than twice that of the second.

In general, the tensile strength of the copolymers goes through a maximum, Young's modulus increases and elongation at the break decreases on irradiation with an electron beam, in the same manner as reported previously,⁷ because of polydiacetylene network formation (Figure 6). The extreme dependence of tensile strength on irradiation may be explained by the internal stress which appears in samples at a certain degree of cross-linking which

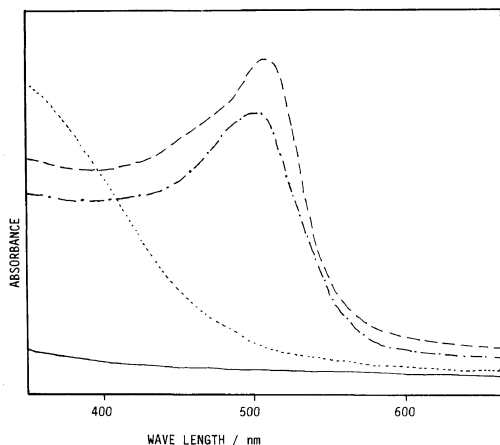


Figure 5. UV-Visible spectra of copolymer A40B60; unirradiated (—), irradiated at 20°C (---), irradiated at 60°C (-·-·-), irradiated at 100°C (····) (50 Mrad).

decreases the tensile strength of the samples. This is confirmed by the behavior of copolymer A80C20. The dependence of tensile strength of this copolymer on irradiation has no maximum but increased continuously with the dose in the region from 0 to 5 Mrad. The degree of crystallinity of A80C20 was much lower than the others and the rate of topochemical cross-polymerization on irradiation is lower since topochemical cross-polymerization took place presumably in the crystalline state. For this reason, even at 5 Mrad, very few diacetylene groups cross-polymerized to induce internal stresses in the sample.

In conclusion, new high molecular weight thermoplastic diacetylene containing polyesters and copolyesters have been synthesized and characterized. The copolyesters had melting transitions temperatures as low as 50°C, and were topochemically cross-linkable on electron beam irradiation. Copolymer A40B60 was found to form a nematic melt and was cross-polymerizable in the liquid-crystalline state to form a polydiacetylene network.

The tensile strength of the copolymers decreased with decrease in crystallinity or melting point of the crystallites and went

through a maximum on irradiation with an electron beam. The electron beam irradiation brought about decrease in elongation at the break and increase in Young's modulus.

The results of this work and the previous work^{6,7} show that, a wide variety of high molecular weight diacetylene-containing polyesters can be synthesized by oxidative coupling reaction under mild conditions. Molecular weight may be further increased by removing water which is the only side product of the polymerization and causes hydrolysis of the ester groups, from the polymerization system. Therefore the mechanical properties may be even more improved. These polyesters are soluble in chlorinated solvents, meltable and can be cast to thin films by spin coating. The diacetylene groups of these polyesters are light sensitive and they undergo radiation-induced topochemical cross-polymerization to form a polydiacetylene network. The third order nonlinear optical susceptibility, $\chi^{(3)}$ of these films is in the range of 10^{-11} — 10^{-10} esu¹¹ and these values are comparable with those reported for Lamgmuir-Blodgett membranes of polydiacetylenes.¹² The polyesters derived from propargyl alcohol are quite economical, and provide interesting new polymeric materials obtainable by chemical reactions of diacetylenic groups such as halogenation, reactions with amines, etc. These topics are currently being investigated, and will be reported in the future.

Acknowledgments. This work was financially supported by Grant No. IN101793 of the Dirección General de Asuntos Personales Académicos (DGAPA). Thanks are also due to C. Vazquez for her assistance in thermal analysis, and A. Maciel for mechanical testing.

REFERENCES

1. D. C. Chemila and J. Zyss, Ed., "Nonlinear Optical Properties of Organic Molecules and Crystals," vol.

- 2, Academic Press, Inc., New York, N.Y., 1987.
2. T. Ogawa and S. Fomin, *Trends in Polymer Science*, **2**, No. 9, 308 (1994).
3. H. Fujiwara and K. Kihara, Jpn. Kokai Tokkyo Koho, JP 01,311,113, 1989 [*Chem. Abst.*, **112**, 218178s (1990)].
4. J. Kato and K. Nakamura, *Nippon Kagaku Kaishi*, 1874 (1988); *ibid.*, 1175 (1989); *ibid.*, 861 (1989).
5. H. Beckham and M. Rubner, *Macromolecules*, **22**, 2130 (1989).
6. S. Fomin, K. Neyra, and T. Ogawa, *Polym. J.*, **26**, 845 (1994).
7. S. Fomin, A. Maciel, and T. Ogawa, *Polym. J.*, **26**, 1270 (1994).
8. S. Dirlikov, Z. Chen, and D. Wang, *Polym. Prepr.*, **33**, 483 (1992).
9. A. S. Hay, D. A. Bolon, K. R. Leimer, and R. F. Clark, *J. Polym. Sci., Polym. Lett.*, **8**, 97 (1970).
10. A. Izuoka, T. Okuno, T. Ito, and T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **226**, 201 (1993).
11. S. Fomine, E. Adem, T. Ogawa, and D. Rao, *Polym. Bull.*, in press.
12. F. Kajzar and J. Mesier, *Thin Sol. Films*, **132**, 11 (1985).