works prepared by anionic polymerization, this influence is localized all around the cross-linked nodules, whereas that of physical entanglements is certainly negligible[1] (Figure 2). On the other hand, the situtation is reversed in the case of radical networks in which the effect of concentration causes a considerable amount of physical entanglements.

We have modified Gibbs and Di Marzio's theory, supposing that, among the $(1 - f)N_2(x - 2)$ zig-zags which are present, a supplementary zig-zags are disposed near to the cross-linking nodules. Their presence, as we have already stated, is imposed by a volume effect among different chains of the same nodule, which depends on the functionality and size of the nodule (Figure 2).

The relation in eq 5 becomes:

$$\frac{1}{x - 2 - a}\left|\frac{v_1}{xv_2}\log v_1 - \log 2x + x - 1\right| = \frac{2e^{-\epsilon/RT_g}}{1 + 2e^{-\epsilon/RT_g}}\frac{\epsilon}{RT_g} + \log\left(1 + 2e^{-\epsilon/RT_g}\right) \quad (6)$$

We have plotted in Figure 3 the variation of T_g against x^{-1} for different values of a according to eq 6. For a given molecular weight $\overline{M}_n$, the cross-linking effect makes the T_g value from the base line $a = 0$ (linear polymer) to the cluster of straight lines $a = 4, 5, 6$ in proportion to the value of the average functionality of the cross-linked nodules. The experimental results corresponding to the dotted lines on Figure 3 are given in Table II. This result reveals clearly the volume effect induced by the cross-links whose influence is very important, as all of the experimental results can be approximately situated between the values $a = 4$ and 6.

These results show that the effect of intermolecular interaction caused by cross-linking can explain quite adequately all of the thermomechanical properties of cross-links of different functionality.

However for a given functionality, the cross-linked networks show a much higher slope than that of star-shaped polymers. This result can be easily explained as in the first case if the chain contains a supplementary zig-zigs at the two chain extremities and in the second case if there are only $a/2$ supplementary zig-zags at the one cross-linked chain extremity. We can then see that the volume effect near the cross-links seems to be less important for the networks than for star-shaped polymers, while the a values are not very different, for a given functionality. This effect can be explained if we consider that star-shaped polymer chains have a much more super-coiled conformation that cross-linked chains and that is why the segment density is higher in the vicinity of this nodule.[1]

References and Notes

(1) F. Rietsch, D. Daveloose, and D. Froelich, *Polymer*, **17**, 859 (1976).
(2) D. J. Worsfold, J. G. Zilliox, and P. Rempp, *Can. J. Chem.*, **47**, 3379 (1969).
(3) P. Weiss, G. Hild, J. Herz, and P. Rempp, *Makromol. Chem.*, **135**, 249 (1970).
(4) J. H. Gibbs and E. A. Di Marzio, *J. Chem. Phys.*, **28**, 373 (1958).
(5) E. A. Di Marzio and J. H. Gibbs, *J. Polym. Sci., Part A-1*, 1417 (1963).
(6) E. A. Di Marzio, *J. Res. Natl. Bur. Stand., Sect. A*, **68**, 611 (1964).
(7) E. A. Di Marzio and J. H. Gibbs, *J. Polym. Sci.*, **40**, 121 (1959).
(8) J. Moacanin and R. Simha, *J. Chem. Phys.*, **45**, 964 (1966).
(9) T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
(10) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
(11) J. H. Gibbs, *J. Chem. Phys.*, **25**, 185 (1956).
(12) K. Onder, R. H. Peters, and L. C. Spark, *Polymer*, **13**, 133 (1972).
(13) H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).

Biphenylene as a Cross-Linking Site in Thermally Stable Polymers

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ABSTRACT: Thermally stable aromatic polymers have been cross-linked by employing the thermal cleavage reaction of biphenylene units incorporated into the polymer chain. Polyamides were synthesized by substituting biphenylene-2,6-dicarboxylic acid chloride for isophthaloylchloride in polymerizations with two different amines. A polybenzimidazole was prepared by substituting dimethyl diphenylene-2,6-dicarboxylate for dimethyl terephthalate in a polymerization with 3,3′,4,4′-tetraaminodiphenyl ether tetrahydrochloride. Polyquinoxalines were synthesized by substituting 2,6-diglyoxalyldiphenylene for dibenzyl derivatives in polymerizations with 3,3′,4,4′-tetraaminodiphenyl ether. The cured polymers showed an increase or disappearance of T_g, complete insolubility, and higher moduli particularly above the T_g.

The introduction of biphenylene in aromatic polyquinolines[1-3] and polyether ketones[4] affords an attractive cross-linking mode because no volatile materials are produced during the cross-linking reaction and the resulting cross-links are thermally stable.

In this study we have investigated the cross-linking reaction of several thermally stable polymers such as polyamides, polybenzimidazoles, and polyquinoxalines containing small amounts of biphenylene in the chain.

Results and Discussion

Monomers. Biphenylene (**1**) and 2,6-diacetylbiphenylene (**2**) were prepared following the procedure described elsewhere[2,5,6] (Scheme I). Biphenylene-2,6-dicarboxylic acid (**3**) was obtained by oxidation of 2,6-diacetylbiphenylene (**2**) with commercial sodium hypochlorite solution. The product was obtained in high yield (89%) when the reaction was carried out at relatively low temperature (40 °C) for 24 h in the presence of tetrabutylammonium hydroxide as a phase-transfer catalyst. Under these conditions, the reaction was complete after 4 h.

The diacid was easily converted with thionyl chloride to biphenylene-2,6-dicarboxylic acid chloride (**4**) which was esterified with methanol to obtain the dimethyl diphenylene-2,6-dicarboxylate (**5**). The selenium dioxide oxidation of 2,6-diacetylbiphenylene (**2**) gave 2,6-diglyoxalyldiphenylene dihydrate (**6**) in 43% yield.

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Scheme I

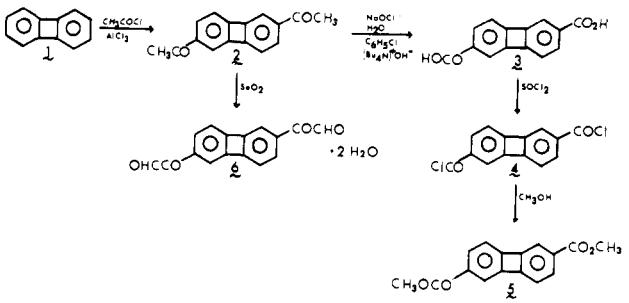

Table I
Properties of Polymers

Polymer	[η] (Solvent)	Elemental Anal.,[b] % C	H	N
7	0.65 (NMP)	71.15	4.24	11.72
		69.87	4.36	11.08
8	1.38 (NMP)	72.97	4.24	8.39
		70.07	4.24	8.28
9	0.23[a] (H_2SO_4 conc)	74.20	3.73	17.17
		72.34	3.81	16.59
10	0.88[a] (*m*-cresol)	81.03	4.07	9.52
		80.05	4.00	9.30
11	0.71[a] (*m*-cresol)	83.25	4.18	9.78
		81.98	4.24	9.30

[a] η_{inh} of a 0.5% solution at 25 °C. [b] Figures in the first row indicate calculated analyses; figures in the second row indicate found analyses.

Polymers. Polyamides **7** and **8** containing small amounts of biphenylene in the chain (2.5%) were synthesized by substituting **4** for isophthaloylchloride in polymerizations with two different amines, *m*-phenylenediamine and 4,4′-diaminodiphenyl ether, in *N*-methylpyrrolidone with propylene oxide as an acid acceptor[7,8] (Scheme II). The polyaromatic benzimidazole **9** was made by substituting **5** for dimethyl terephthalate in polymerization with 3,3′,4,4′-tetraaminodiphenyl ether tetrahydrochloride in polyphosphoric acid at 200 °C (Scheme II). Polyquinoxalines **10** and **11** were synthesized by substituting **6** for dibenzyl derivatives in polymerizations with 3,3′,4,4′-tetraaminodiphenyl ether in a 1:1 mixture of *m*-cresol–xylene at room temperature[10] (Scheme II). Some characteristics of the polymers are summarized in Table I.

Cross-Linking Studies. The DSC and TMA cells were used to cure samples of polymer film. After curing, the T_g of the samples were recorded as well as their thermal behavior up to 400 °C. In all cases the magnitude of the deflection at T_g in the cured samples was sharply reduced compared to those recorded during the heating period up to the curing temperature. The samples were completely insoluble after curing 3 h at 380 °C; however, the DSC trace still exhibited an intense exothermic peak after curing (Table II).

The dynamic mechanical properties of uncured and cured films of polyamides **7** and **8** and polyquinoxalines **10** and **11** (Table III) were obtained from room temperature to 450 °C.

In the case of polybenzimidazole **9** no T_g was visible by DSC at the highest sensitivity of the instrument. Modulus measurements were not made since good films could not be obtained as a result of the poor solubility of the polymer in the common organic solvents. Thus the cross-linking could be followed only by its solubility before and after curing. The uncured polybenzimidazole was soluble in concentrated sulfuric acid and partially soluble in Me_2AC, Me_2SO, and DMF. After curing 3 h at 380 °C the polymer sample was completely insoluble in Me_2SO, DMF, and Me_2AC, but it required 6 h of curing to achieve insolubility in concentrated sulfuric acid. The Young's modulus of films are relatively constant up to the glass transition temperature both for polyamides (Figure 1) and polyquinoxalines (Figure 2). A major relaxation occurs in the glass transition interval, resulting in a decrease of E' from the order of 10^{10} to 10^7–10^8 dyn/cm^2.

In the case of polyamide **7** the E' above T_g was found to have a value of 2.8×10^9 and the polymer could not be cured at temperatures higher than 340 °C because broken films resulted. These facts provide some evidence that this polymer maintains a high degree of crystallinity even after the intro-

Scheme II

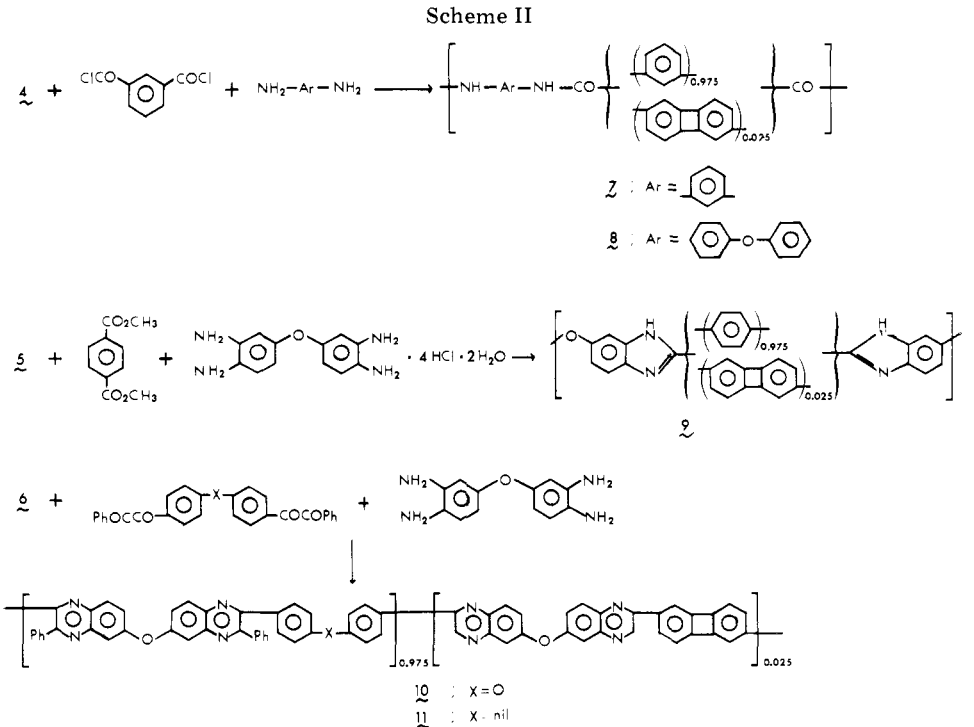

Table II
Curing of Polyamides 7 and 8 and Polyquinoxalines 10 and 11

Polymers	T_g(DSC), °C	T_g(TMA), °C	Onset of exothermic[a] peak above T_g, °C	Curing conditions		Cured	
				Temp, °C	Time, h	T_g(DSC), °C	T_g(TMA), °C
7	252	245	313	340	1	258	275
				340	3	269	313
				340	6	271	313
8	230	225	298	380	1	245	290
				380	3	250	358
				380	6	270	*b*
10	244	240	325	380	1	259	290
				380	3	261	*b*
				380	6	264	*b*
11	249	270	315	380	1	274	365
				380	3	280	*b*
				380	6	290	*b*

[a] Defined at the intercept of an extrapolated baseline above T_g with the tangent of the slope. [b] No detectable T_g.

Table III
Thermomechanical Properties of Polymers

Polymer	T_g(DSC), °C	T (E''_{max}), °C	E'(25 °C), dyn/cm²	E' above T_g,[d] dyn/cm²
7[f]	252	248[b]	2.3×10^{10}	2.8×10^{9}
		305	3.0×10^{10}	8.1×10^{9}
8[a]	230	216[b]	2.5×10^{10}	2.3×10^{8}
		323	2.7×10^{10}	8.1×10^{9}
10[a]	244	253[c]	2.3×10^{10}	*e*
		316	2.6×10^{10}	1.4×10^{8}
11[a]	249	270[c]	1.9×10^{10}	*e*
		372	2.0×10^{10}	2.4×10^{8}

[a] Figures in the first row indicate thermomechanical properties of uncured samples; figures in the second row indicate thermomechanical properties of a sample cured for 4 h at 350–380 °C. [b] Applied frequency, 110 Hz. [c] Applied frequency 35 Hz. [d] E' above T_g was measured at a temperature above that on which the rapid decrease in E' had stopped. [e] Unable to obtain even at the highest instrument sensitivity. [f] Figures in the second row indicate thermomechanical properties of a sample cured at 4 h at 320–340 °C.

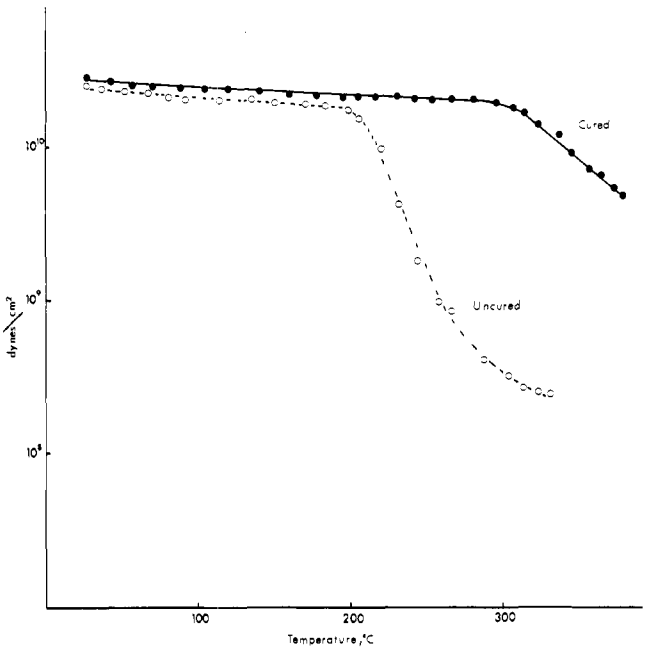

Figure 1. Dynamic tensile modulus E' before and after curing 4 h at 350–380 °C vs. temperature for polyamide 8.

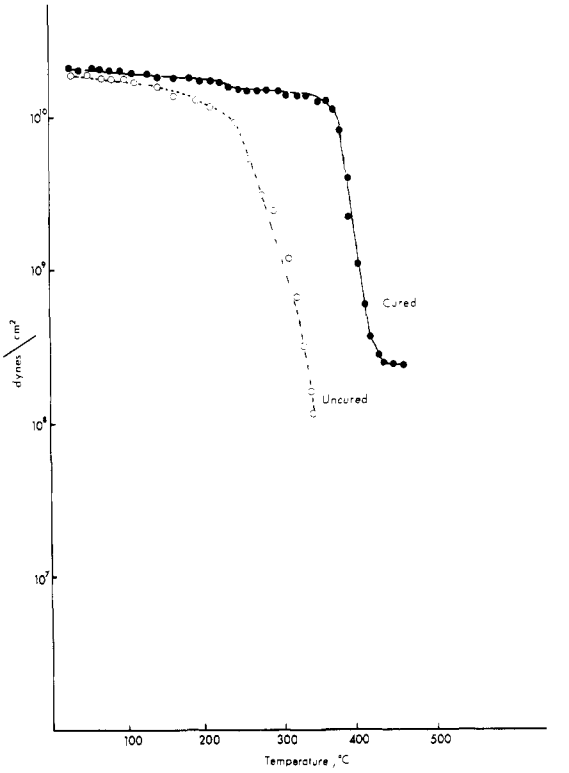

Figure 2. Dynamic tensile modulus E' before and after curing 4 h at 350–380 °C vs. temperature for polyquinoxaline 11.

duction of biphenylene in the chain.[11] Correlations between DSC, TMA, and the maximum in the loss modulus (E'') were relatively good for all the polymers (Table III). The effects of curing on the dynamic storage moduli are shown in Table III and Figures 1 and 2. The sharp decrease in the dynamic storage moduli representing the T_g of polyquinoxalines void of biphenylene units is progressively shifted toward higher temperatures by heating the films at 400 °C in an inert atmosphere.[12] This effect was attributed to pyrolitic cross-linking. However, introduction of biphenylene in the polymer chain allows the use of lower curing temperatures (350 °C vs. 400 °C) and lower curing times (4 h vs. 8 h) to give a material that undergoes a maximum in loss modulus at higher temperatures, and has a higher modulus, especially above the T_g (Table III, Figure 2). It is instructive to note also that within the two polyquinoxalines 10 and 11 studied here, the cross-linking does not have the same efficiency. In fact, in polymer

11 a large increase in the T_g (365 °C vs 270 °C) is observed by TMA after curing for 1 h at 380 °C, and this is in accordance with the very high temperature at which the maximum in the loss modulus is observed after curing film samples (372 °C vs. 270 °) (Table III, Figure 2). Such a high increase in the T_g is not observed in polymer **10** (Table II and III). There is no obvious explanation for this difference, but it is apparent that with polymers containing such a small percentage of biphenylene units in the chain, the cross-linking probably occurs through a series of radical abstraction and coupling reactions, rather than tetrabenzocyclooctatetraene formation (dimerization). The radical reaction appears to be more favored in polymer **11** containing biphenyl than in polymer **10** containing diphenyl ether. Studies on the mechanism of this cross-linking reaction are in progress.

In every case, the thermal stability of films of polymer samples, as measured by thermal gravimetric analysis, was about the same for the cured samples as that reported for samples of polymers not containing the biphenylene units. For example, both samples of cured polyquinoxalines **10** and **11** showed breaks in air and nitrogen at 530 and 550 °C, respectively, showing 15–20% weight loss under nitrogen at 700 °C. This TGA behavior is the same as that reported for analogous polyquinoxlines without the biphenylene units.[13]

Conclusion

As anticipated,[2] efficient thermally induced cross-linking occurs in thermally stable polymers such as polyquinoxlines, polyamides, and polybenzimidazoles containing low contents of biphenylene in the chain. The cross-linking reaction affords complete insolubility, a higher T_g or disappearance of the T_g, and a higher modulus especially above the T_g.

Experimental Section

Biphenylene (1) and 2,6-Diacetylbiphenylene (2). These compounds were prepared following the procedures described elsewhere.[2,5,6]

Biphenylene-2,6-dicarboxylic Acid (3). A solution of 70 mL of commercial sodium hypochlorite and 1.3 g of a 25% methanol solution of tetrabutylammonium hydroxide was warmed to 40 °C and 0.91 g (3.8 mmol) of 2,6-diacetylbiphenylene in 30 mL of warm chlorobenzene was added.

The two layers were vigorously stirred at 40 °C for 24 h and the insoluble product was filtered and washed, first with sodium hydrosulfite solution and then with dilute hydrochloric acid. After drying in vacuo 0.81 g (88%) of the dicarboxylic acid was obtained, mp 280 °C dec. The acid was partially purified by dissolution in concentrated ammonium hydroxide solution and reprecipitation with dilute hydrochloric acid; IR (KBr) 3000 and 1670 cm^{-1}. Anal. Calcd for $C_{14}H_8O_4$: C, 70.00; H, 3.36. Found: C, 66.85; H, 3.50.

Biphenylene-2,6-dicarboxylic Acid Chloride (4). A mixture of 10 mL of thionyl chloride, 0.7 g (2.9 mmol) of biphenylene-2,6-dicarboxylic acid, and two drops of pyridine was heated to the reflux temperature for 8 h and then the solution was left overnight at room temperature. The thionyl chloride was removed under reduced pressure at 40–50 °C. The dried crude product was recrystallized two times from benzene to yield 0.39 g (47%) of the monomer: mp 242–244 °C; IR (KBr) 1740 cm^{-1}. Anal. Calcd for $C_{14}H_6O_2Cl_2$: C, 60.68; H, 2.18. Found: C, 60.12; H, 2.26.

Dimethyl Biphenylene-2,6-dicarboxylate (5). A mixture of 10 mL of thionyl chloride, 0.5 g (2 mmol) of biphenylene-2,6-dicarboxylic acid, and two drops of pyridine was heated to the reflux temperature for 8 h, and then the solution was left overnight at room temperature. The thionyl chloride was removed under reduced pressure at 40–50 °C. The dried crude product was then dissolved in 30 mL of hot carbon tetrachloride and 5 mL of dried methanol was added. The solution was stirred for 24 h at 60 °C in the presence of 0.5 mL of pyridine. The solution was then filtered and allowed to cool at room temperature. The insoluble solid was collected by filtration and recrystallized from benzene, giving 0.53 g (94%) of crystals: mp 223–225 °C; IR (BKr) 1712 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.47; H, 4.51.

2,6-Diglyoxalyldiphenylene Dihydrate (6). To a solution of 1.23 g (1.1 mmol) of selenium dioxide in 60 mL of acetic acid and 1 mL of water containing one drop of hydrochloric acid was added 1.18 g (5 mmol) of 2,6-diacetylbiphenylene. The mixture was heated at the reflux temperature for 4 h, during which time the selenium metal precipitated. The hot mixture was then filtered and the red filtrate was allowed to cool at room temperature. The insoluble solid was collected by filtration, dissolved in 100 mL of dioxane, and stirred overnight with 1 g of charcoal to remove the red selenium metal. After gravity filtration the dioxane was removed under reduced pressure and the residue was recrystallized from a 50:50 mixture of water–dioxane to yield 0.64 g (43%): mp 206 °C dec; IR (KBr) 3410, 1690, 1720 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_6$: C, 64.00; H, 4.03. Found: C, 63.97; H, 3.77.

Polymerizations. *m*-Phenylenediamine, 4,4′-diaminodiphenyl ether, and 3,3′,4,4′-tetraaminodiphenyl ether were purified by sublimation under reduced pressure. Tetraaminodiphenyl ether tetrahydrochloride was purified by recrystallization under a nitrogen atmosphere from water–hydrochloric acid. A general procedure for the polymerization reactions in each system follows:

Polyamide 8. The polymerization flask was charged under nitrogen with 1.005 g (5 mmol) of diaminodiphenyl ether and 20 mL of dry NMP. After cooling the solution to 0 °C, 1.5 mL of propylene oxide was added. The mixture was then cooled to −25 to −30 °C and with vigorous stirring 0.992 g (4.875 mmol) of isophthaloyl chloride and 0.35 g (0.125 mmol) of biphenylene-2,6-dicarboxylic acid chloride **4** was added; 5 mL of dry NMP was used to wash the dichlorides from the addition funnel. The solution was stirred at this temperature for 1 h and then for 4 h at room temperature. The solution obtained was slowly poured into a large volume of methanol (300 mL) with vigorous stirring. The white polymer was collected by filtration, washed well with methanol (three to four times), and dried under reduced pressure. The polycondensation reaction of polyamide **7** was carried out in NMP/propylene oxide under the same conditions. The elemental analyses are given in Table I. Films were cast from 15% NMP solution in the presence of 3% of LiCl.

Polybenzimidazole 9. To 70 g of PPA (116%) was added gradually under nitrogen at 140 °C 2.059 g (5 mmol) of tetraaminodiphenyl ether tetrahydrochloride. During the addition bubbles of hydrogen chloride gas were purged by the nitrogen stream. To this solution was added 0.947 g (4.875 mmol) of dimethyl terephthalate and 0.0335 g (0.125 mmol) of dimethyl diphenylene2,6-dicarboxylate (**5**). Heating was maintained at 200 °C for 15 h. The polymer was isolated by pouring the hot solution into water, and the precipitate was washed with water by decantation. The polymer was then slurried in dilute sodium bicarbonate solution overnight and washed thoroughly with water and methanol. The polymer was dried at 100 °C under reduced pressure for 3 days. The elemental analysis is given in Table I.

Polyquinoxaline 10. To a stirred slurry of 0.576 g (2.5 mmol) of 3,3′,4,4′-tetraaminodiphenyl ether in a 1:1 mixture of *m*-cresol and xylene (10 mL) was added 1.059 g (2.1 mmol) of 4,4′-oxydibenzyl and 0.0188 g (0.05 mmol) of 2,6-diglyoxalylbiphenylene dihydrate (**6**) as powders over a 3-min period. Additional solvent (2 mL) was used to wash residual monomers into the reaction pot and the reaction temperature was maintained at 35 °C by cooling in a water bath. The reaction mixture was stirred at ambient temperature for 18 h to yield a yellowish-brown viscous solution. A portion of the solution was poured into methanol to yield a fibrous light yellow polymer which was washed with hot methanol and dried under reduced pressure. Films were prepared by doctoring the polymer solution onto plate glass followed by drying in a forced air oven at 70 °C for 5 h. The films were then dipped in ethanol–triethylamine mixture overnight and then dried at 100 °C under reduced pressure.

The polycondensation reaction of polyquinoxaline 11 was carried out in *m*-cresol–xylene, under the same conditions. The elemental analyses are given in Table I.

Glass Transitions, Thermomechanical Analyses, and Thermogravimetric Analyses. Thermal transitions were measured using a Differential Scanning Calorimetry Cell attachment for a Du Pont 990 Differential Thermal Analyzer, under 40 mL/min flow of nitrogen and at a heating rate of 20 °C/min, the reference being glass beads.

Thermomechanical analyses (TMA) were conducted on film samples of the polymers using a Du Pont 990 and 943 Thermomechanical Analyzer at a heating rate of 5 °C/min.

The dynamic mechanical properties of samples were determined as follows using the Rheovibron (Model DDV-II): Samples were cut into narrow strips approximately 3 cm in length, 0.3 cm in width, and 0.002 cm in thickness. Runs were made at a frequency of 110 Hz at a heating rate of 5 °C/min in an inert sample atmosphere. The dynamic moduli of films were calculated using the following equation:

$$|E^*| = \frac{2}{(A)(\mathrm{DF} - K)} \frac{L}{S} \times 10^9 \text{ dyn/cm}^2$$

Where A is a constant given by the instrument manual,[14] DF is the value of the dynamic force dial when measuring tan δ, L is the length of sample, S is the cross-sectional area in cm^2, and K is an error constant due to the modulus of electricity and displacement of the stress gauge. Values of Young's modulus E' and the loss modulus E'' were obtained as follows:

$$E' = |E^*| \cos \delta$$

and

$$E'' = |E^*| \sin \delta$$

Thermal gravimetric analyses were carried out on thin films using a Du Pont 950 thermal balance and a 990 thermal analyzer (recorder). Samples were heated at a rate of 5 °C/min under air and nitrogen atmospheres.

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References and Notes

(1) J. Garapon, W. H. Beever, and J. K. Stille, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18**, 138 (1977).
(2) J. Garapon and J. K. Stille, *Macromolecules*, **10**, 627 (1977).
(3) A. Recca, J. Garapon, and K. K. Stille, *Macromolecules*, **10**, 1344 (1977).
(4) R. J. Swedo and C. S. Marvel, private communication.
(5) F. M. Longullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, **48**, 12 (1968).
(6) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).
(7) C. Chiriac and J. K. Stille, *Macromolecules*, **10**, 710 (1977).
(8) C. Chiriac and J. K. Stille, *Macromolecules*, **10**, 712 (1977).
(9) Y. Iwakura, K. Uno, and Y. Imai, *J. Polym. Sci., Part A-1*, **2**, 2605 (1964).
(10) P. M. Hergenrother, *Macromol. Synth.*, **5**, 17 (1974).
(11) H. Kakida, Y. Chatani, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **14**, 427 (1976).
(12) W. Wrasidlo, *J. Polym. Sci., Part A2*, **9**, 1603 (1971).
(13) P. M. Hergenrother, *J. Macromol. Sci., Rev. Macromol. Chem.*, **c6(1)**, 1 (1971).
(14) Rheovibron Model DDV-II Instruction Manual 14, August, 1969, Tape Measuring Instrument Co., Ltd.

Asymmetric Induction by Copolymerization of Indene with Acrylic Acid in the Presence of Lecithin

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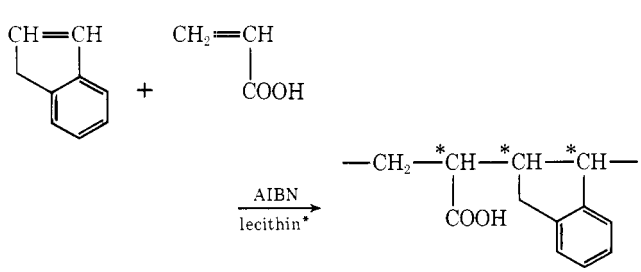
ABSTRACT: The copolymerization of indene with acrylic acid was studied in the presence and absence of lecithin, using 2,2′-azobis(isobutylo)nitrile (AIBN) in benzene. The rate of copolymerization was found to be enhanced by addition of lecithin. Further, a slightly optically active copolymer was obtained in the presence of lecithin. The sign of the optical rotation of the copolymer was opposite to that of lecithin. The optical activity is thought to be due to the asymmetry induced to the backbone of the copolymer by the chirality of lecithin. The asymmetric induction copolymerization can be explained on the basis of the electrostatic interaction between acrylic acid and the polar head group of lecithin.

In our previous papers, it was revealed that the chiral surface active substance, lecithin, acts as an asymmetric inducing agent in oil/water interfacial systems[1,2] and in homogeneous copolymerization systems.[3,4] In benzene solutions containing lecithin, styrene (St) and indene (IN) were ascertained to copolymerize with maleic anhydride (MAn) to give corresponding alternating copolymers with significant optical activities.[3,4] It was concluded that the asymmetric inductions were caused by electrostatic interaction between the polar monomer, MAn, and the polar head group of the chiral surface active substance, lecithin. Thus, the nonpolar vinyl monomer, St (or the nonpolar α,β-disubstituted olefin, IN), copolymerized with the polar α,β-disubstituted olefin, MAn, affected by lecithin micelle.

Now then, if there is an electrostatic interaction between a polar vinyl monomer and the polar head group of lecithin, it seems possible to obtain an optically active copolymer by the copolymerization of a nonpolar α,β-disubstituted olefin with a polar vinyl monomer in the presence of lecithin.



This paper describes the asymmetric induction copolymerization of IN with acrylic acid (AAc) in the presence of lecithin.

Experimental Section

Materials. Lecithin (from soy beans) was supplied by the Katayama Chemical Co. Ltd. and used without further purification: $[\alpha]_D$ +8.71° (c 2.40, THF), λ_0 = 148 nm, $\bar{M}_w$ = 780. Indene (IN) and acrylic acid (AAc) were obtained commercially, purified by the usual methods, and distilled under reduced pressure in a stream of nitrogen just before use. 2,2′-Azobis(isobutylo)nitrile (AIBN) was purified by recrystallization from methanol. Benzene and other organic solvents were purified by the conventional methods.

Polymerization Procedure. The copolymerization of IN with AAc was carried out in benzene in a sealed tube, using AIBN as an initiator. The prescribed amounts of IN, AAc, AIBN, lecithin, and benzene were mixed in a glass tube. The tube was flushed three times with nitrogen, sealed in vacuo, and shaken in a thermostated incubator. After a definite time of polymerization, the tube was cooled in a dry ice/methanol bath to stop the polymerization. After tapping the tube, the contents were added to a large amount of n-hexane. The precipitated copolymer was filtered off and dried in vacuo. The copolymer was purified by treatment with an aqueous solution. Thus, the copolymer was dissolved in 2 N NaOH with stirring and then acidified with 5 N HCl to precipitate the copolymer. The copolymer precipitated was filtered off, washed with distilled water, dried in vacuo, and subjected to optical measurements. The purification procedure was repeated until there was no change in specific rotation of the copolymer.

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