of crown compounds increases much more slowly (Table I), end-to-end cyclization will contribute very little to the formation of macrocycles.

It is interesting to compare acid-catalyzed polymerizations of THF and dioxolane. The apparent differences between both systems have been pointed out repeatedly.[14,15] In view of the present discussion, some similarities become evident: in both cases, the concentration of end groups is very low, in both cases macrocyclic oligomers are formed,[16] and in both cases the number of end groups is consequently much smaller than would be expected for the number of polymer molecules.[14]

The polymerization of dioxolane with proton acids might therefore involve a similar sequence of chain coupling–ring opening steps. Such a mechanism would explain the presence of macrocycles, the absence of linear oligomers, and the very low concentration of end groups normally found in acid-catalyzed dioxolane polymerizations.[15,17]

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Asymmetric Induction by Copolymerization of Indene with Maleic Anhydride in the Presence of Lecithin

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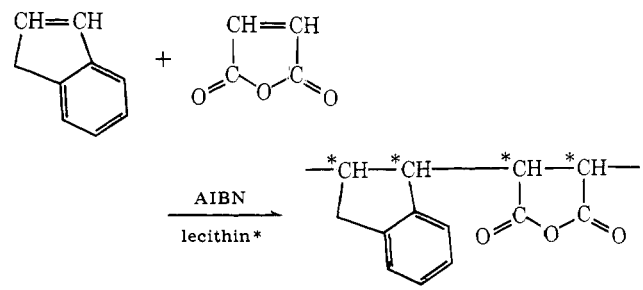
ABSTRACT: The copolymerization of indene (IN) with maleic anhydride (MAn) was studied in the presence and absence of lecithin as a chiral surface active substance, using 2,2′-azobis(isobutylonitrile) (AIBN) in benzene. The rate of copolymerization and intrinsic viscosity of the resulting copolymer were observed to be lowered by lecithin. Moreover, it was found that IN copolymerizes with MAn to give an alternating copolymer and that an optically active copolymer is formed by addition of lecithin to the copolymerization system. The optical activity observed is presumed to be due to asymmetry induced in the backbone of the copolymer by the chirality of lecithin. The influence of lecithin on the copolymerization is considered to be caused by an electrostatic interaction between MAn and the polar head group of lecithin.

In previous papers, the authors revealed that lecithin acts as an asymmetric inducing agent in oil/water interfacial emulsion systems, in which some water-insoluble and unsymmetric ketones are reduced asymmetrically with an aqueous $NaBH_4$ solution[1] and styrene copolymerizes stereospecifically with maleic acid dissolved in an aqueous phase to give an optically active copolymer.[2] It was concluded that these asymmetric inductions are based almost entirely on stereochemical controls at the micelle–water interface, in the vicinity of which the asymmetric carbon atom of lecithin is present.

Moreover, an asymmetric induction was achieved under water-free conditions. Thus, an optically active copolymer was obtained by copolymerization of a nonpolar vinyl monomer, styrene (St), with a polar α,β-disubstituted olefin, maleic anhydride (MAn), in the presence of a chiral surface active substance, lecithin.[3] The authors concluded that in the copolymerization of St with MAn in the presence of lecithin the polar monomer (MAn) is captured within the reversed lecithin micelle, in which an electrostatic interaction between MAn and the polar head group of lecithin is present, and that the asymmetric induction proceeds via CT complex of St and MAn affected by the chiral surface active (amphiphilic) substance, lecithin. It is attractive to examine possibilities of asymmetric induction copolymerization of other nonpolar monomers with other polar monomers in the presence of lecithin.

This paper deals with the asymmetric induction copolymerization of a nonpolar α,β-disubstituted olefin, indene (IN),



with a polar α,β-disubstituted olefin, maleic anhydride (MAn), in the presence of lecithin.

Experimental Section

Materials. Lecithin (from soy beans) was supplied by the Katayama Chemical Co. Ltd. and was used without further purification. $\bar{M}_w$

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Table I
Copolymerization of Indene (M_1) with Various Polar Monomers (M_2) in the Presence of Lecithin [a]

M_1, mol L^{-1}	M_2, mol L^{-1}	Polymn time, h	Yield of polym, g	$[m_1]/([m_1]+[m_2])$ [c]	$[\alpha]_D$ [d]	λ_0, nm
IN, 1.72	MAn, 1.72 [b]	36	0.502	0.47	+4.02 (+0.72 [e])	206 (203 [e])
IN, 1.72	AAc, 1.72	114	0.501	0.30	−0.45 [f]	
IN, 1.72	MMA, 1.87	24	1.004	0.17	0.00	
IN, 1.72	DMM, 1.60	24	0.604	0.57	0.00	
IN, 1.72	VP, 1.72	180	0.120	0.73	0.00	
IN, 1.72	AN, 1.72	66	0.416	0.37	0.00	
IN, 0.86	FN, 0.86	114	0.241	0.45	0.00	

[a] [AIBN] = 1.0×10^{-3} mol L^{-1} and [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene. Total volume, 10 mL. Polymerization temperature, 40 °C. IN = indene, MAn = maleic anhydride, AAc = acrylic acid, MMA = methyl methacrylate, DMM = dimethyl maleate, VP = 1-vinyl-2-pyrrolidinone, AN = acrylonitrile, FN = fumaronitrile. [b] [AIBN] = 1.0×10^{-3} mol L^{-1}. [c] Determined by elemental analysis. [d] Measured in THF at 25 °C. [e] Measured for the hydrolyzed copolymer in methanol at 25 °C. [f] $[\alpha]_{400}$ measured in methanol.

= 780, $[\alpha]_D$ +8.71° (*c* 2.40, THF). Indene (IN) was purified by the usual method[4] and distilled under reduced pressure in a stream of nitrogen before use. Commercially available maleic anhydride (MAn) was purified by recrystallization from water-free chloroform. Other monomers, i.e., acrylic acid, methyl methacrylate, dimethyl maleate, 1-vinyl-2-pyrrolidinone, acrylonitrile, and fumaronitrile, were supplied commercially and purified by distillation before use. 2,2′-Azobis(isobutylonitrile) (AIBN) was purified by recrystallization from methanol. Benzene and other organic solvents were purified and dehydrated by conventional methods before use.

Polymerization Procedure. The copolymerization of IN with MAn was carried out in a sealed tube, using AIBN as an initiator. The prescribed amounts of IN, MAn, 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 polymerization time, the tube was cooled in a dry ice/methanol bath to stop the polymerization. After breaking the tube, the contents were added to a 1:2 mixture of benzene and *n*-hexane. The precipitated copolymer was filtered off, dried in vacuo, and purified by reprecipitation from a THF solution with a large quantity of *n*-hexane. The purification of the optically active copolymer was repeated until there was no change in specific rotation.

The copolymerization of IN with the other monomers was conducted in the same manner as described above.

Hydrolysis of the Optically Active IN/MAn Copolymer. Optically active IN/MAn copolymer (0.5 g) was dissolved in 50 mL of 2 N NaOH solution with vigorous stirring at room temperature. The solution was stirred continuously for 20 h and then acidified with 50 mL of 5 N HCl solution to precipitate the hydrolyzed copolymer. The precipitated copolymer was filtered, washed with a large amount of water, dried in vacuo, and subjected to optical measurement.

Physical Measurements. Intrinsic viscosity of the copolymers was measured in THF at 30 °C, using an UBBELOHDE type viscometer. D-line optical rotation and optical rotatory dispersion (ORD) measurements were carried out with a Jasco Model J-20 automatic recording spectropolarimeter equipped with a xenon source. IR spectra of the copolymers were obtained on a Jasco Model IRA-2 Grating IR spectrometer. UV spectra were measured by means of a Hitachi Model 200-10 spectrophotometer using 1-mm quartz cells at 25 °C; a continuous variation method[5] was adopted for the sake of determination of the composition of the charge-transfer complex of IN with MAn.

Results and Discussion

Copolymerization of Indene (M_1) with Various Polar Monomers (M_2). The nonpolar α,β-disubstituted olefin, indene (IN), was copolymerized with various polar monomers, i.e., maleic anhydride (MAn), acrylic acid (AAc), methyl methacrylate (MMA), dimethyl maleate (DMM), 1-vinyl-2-pyrrolidinone (VP), acrylonitrile (AN), and fumaronitrile (FN), using 2,2′-azobis(isobutylonitrile) (AIBN) as an initiator in the presence of lecithin in benzene. The conditions and results of the copolymerizations are summarized in Table I.

The copolymer of IN with MAn was found to be optically active. Optical activity was observed even after hydrolysis of the optically active IN/MAn copolymer. The optical activity observed for the copolymer is presumed to be caused by asymmetry induced to the backbone of the copolymer by the chirality of lecithin. ORD measurements for the IN/MAn copolymer and its hydrolyzed copolymer gave corresponding positive plain curves as shown in Figure 1. The λ_0 values (206 and 203 nm) of the copolymers calculated using the simple Drude equation[6] were close to λ_{max} of the UV absorption band of the carbonyl group of MAn, 212 nm. These λ_0 values indicate that the asymmetry is induced to the side of MAn monomer units of the chain backbone of the IN/MAn copolymer.

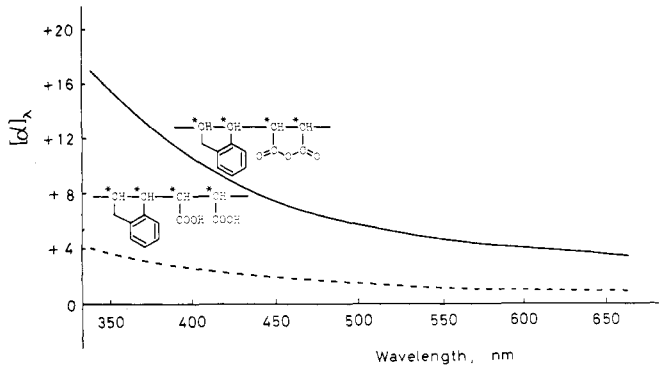

Figure 1. Optical rotatory dispersion (ORD) curves for the IN/MAn copolymer (solid curve) and its hydrolyzed copolymer (broken curve).

The copolymerization of IN with AAc gave a slightly optically active copolymer, the optical rotation of which was of opposite sense to that of lecithin. No optical activity was observed for the copolymers of IN with MMA, DMM, VP, AN, and FN.

These results indicate that MMA, DMM, VP, AN, and FN are not affected by lecithin and exist, rather, in the exterior of the reversed lecithin micelle and that the copolymerizations proceed without influence of the chirality of lecithin. However, MAn and AAc are considered to be affected by the polar head group of lecithin. The asymmetric induction copolymerization of IN with MAn by lecithin will hereinafter be described.

Influence of Variation in Monomer Ratio. The copolymerization of IN with MAn was carried out under conditions of a constant molar concentration of the total monomer in the presence of a constant amount of lecithin and in its absence. The conditions and results of the copolymerization are summarized in Table II and illustrated in Figure 2.

The IR spectra of the optically active copolymers obtained in the presence of lecithin were the same as the optically inactive copolymers obtained in its absence.

It is well known that MAn copolymerizes with some elec-

Table II
Copolymerization of Indene (IN, M_1) with Maleic Anhydride (MAn, M_2) [a]

$[M_1]$, mol L^{-1}	$[M_2]$, mol L^{-1}	$10^6 Rp$, mol L^{-1} s^{-1}	$[m_1]/([m_1] + [m_2])$ [d]	$10^{-2}[\eta]$, [e] cm^3 g^{-1}	$[\alpha]_D$ [f]
0.431	3.017	10.74 [b]	0.47	0.91	0.00
		1.02 [c]	0.45	0.40	+4.25
0.862	2.586	13, 45 [b]	0.46	0.90	0.00
		2.27 [c]	0.45	0.51	+3.65
1.293	2.155	13.46 [b]	0.46	0.87	0.00
		2.91 [c]	0.46	0.62	+4.13
1.724	1.724	9.25 [b]	0.47	0.78	0.00
		3.61 [c]	0.45	0.60	+4.60
2.155	1.293	6.63 [b]	0.49	0.68	0.00
		3.27 [c]	0.46	0.55	+4.33
2.586	0.862	3.83 [b]	0.48	0.51	0.00
		2.54 [c]	0.48	0.47	+1.86
3.017	0.431	1.40 [b]	0.50	0.38	0.00
		0.86 [c]	0.48	0.34	+0.27

[a] [IN] + [MAn] = 3.448 mol L^{-1} and [AIBN] = 1.0×10^{-3} mol L^{-1} in benzene. Total volume, 10 mL. Polymerization temperature, 40 °C. [b] In the absence of lecithin. Polymerization time, 12 h. [c] In the presence of lecithin. [lecithin] = 6.41×10^{-2} mol L^{-1}. Polymerization time, 24 h. [d] Determined by elemental analysis. [e] Measured in THF at 30 °C. [f] Measured in THF at 25 °C.

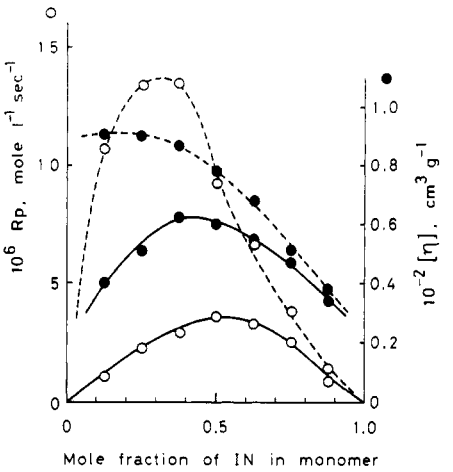

Figure 2. Influence of monomer ratio on the rate of copolymerization (○) and intrinsic viscosity (●) of the copolymer. [IN] + [MAn] = 3.448 mol L^{-1}, [AIBN] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene. Temperature, 40 °C; time, 24 h. (- - -) In the absence of lecithin.

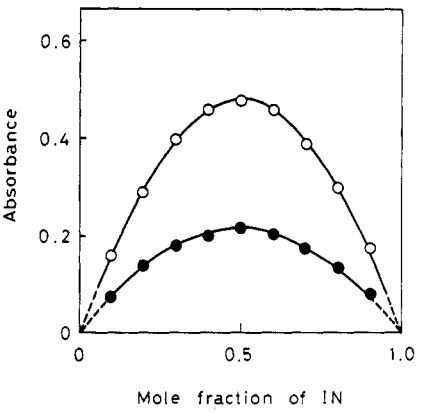

Figure 3. Continuous variation method in UV spectra for the absorbance due to the charge-transfer complex of indene (IN) with maleic anhydride (MAn) in benzene solution at 25 °C: (○) λ 350 nm; (●) λ 370 nm. [IN] + [MAn] = 0.50 mol L^{-1}; cell length, 1 mm.

tron-donor monomers such as styrene,[7] vinyl ether,[8] and benzofuran[9] to give alternating copolymers independent of the monomer ratio. This behavior has been explained on the basis of charge-transfer complex of the two monomers. It is predictable that IN also forms CT complex with MAn. The presence of CT complex was detected by means of UV spectra, using a continuous variation method.[5] Figure 3 shows the formation of a 1:1 type complex of IN with MAn.

It is clear from Table II that the copolymer composition is independent of the IN/MAn composition in monomer feed and that every copolymer is alternating. This result indicates that the copolymerization proceeds via a CT complex of IN and MAn even in the presence of lecithin. Optically active copolymers were obtained by the copolymerization in the presence of lecithin. The specific rotation of the resulting copolymer was approximately constant regardless of the monomer composition except at high mole fraction of IN in the monomer feed. The low specific rotation of the copolymer obtained from the system with a high mole fraction of IN in monomer feed indicates that the copolymerization proceeds, under the conditions, merely at the exterior of the lecithin micelle, in which no interaction between MAn and the polar head group of lecithin is present. The optical data were consistent with the kinetic behavior of the copolymerization. That is to say, when the mole fraction of IN was low, i.e., MAn concentration was high, the rate of copolymerization was lowered strongly and gave a copolymer with high optical activity. On the contrary, when the mole fraction of IN was considerably high, i.e., MAn concentration was low, the rate of copolymerization was lowered slightly and a slightly optically active copolymer was obtained.

The ORD measurements for these optically active copolymers gave positive plain curves, from which λ_0 values were calculated as 202 to 208 nm. The intensity of the specific rotation of the copolymer was independent of the solvent used for the optical measurement.

As can be seen from Figure 2, the maximum point of the rate of copolymerization appeared at a higher concentration of MAn in monomer feed in the absence of lecithin. It is considered that in the system IN/MAn the copolymer radical consisting of IN unit in the active chain end is more stable than that consisting of MAn unit in the active chain end. This result is different from that observed for the copolymerization of St with MAn, in which the maximum point of the rate of copolymerization appears at an equimolar concentration of the two monomers.[10] This difference is considered to be due to the difference in reactivities of St and IN toward copolymerization with MAn via a CT complex. In the presence of lecithin, however, the maximum point of the rate of copoly-

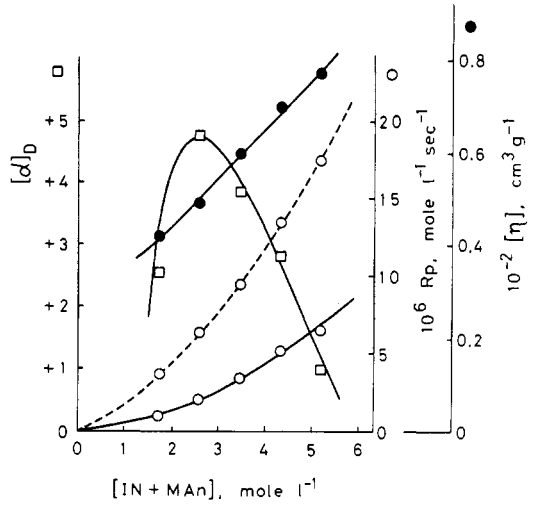

Figure 4. Influence of monomer concentration on the rate of copolymerization (○), intrinsic viscosity (●), and specific rotation (□) of the copolymer. [IN] = [MAn], [AIBN] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene. Temperature, 40 °C; time, 36 h. (-○-) In the absence of lecithin.

merization of IN with MAn appeared near the equivalent concentration of the two monomers. The absolute value of the rate of copolymerization was depressed, especially at a high mole fraction of MAn in monomer feed, by the addition of lecithin as observed for the copolymerization of St with MAn.[3] This retardation effect of lecithin on the rate of copolymerization also seems to be due to the "capture" of MAn within the reversed lecithin micelle. The intrinsic viscosity of the copolymer varied with the rate of copolymerization as a function of mole fraction of IN in the monomer feed.

Influence of Monomer Concentration. IN was copolymerized with MAn in the presence of a constant amount of lecithin and in its absence. The molar concentration of IN was made equal to that of MAn in the monomer feed. The conditions and results of the copolymerization are illustrated graphically in Figure 4.

The rate of copolymerization increased exponentially with an increase in monomer concentration. As shown in Figure 5, the plots of log ([IN] + [MAn]) vs. log *Rp* gave straight lines with different slopes. From the slopes of these straight lines, the rate of copolymerization was found to be proportional to 1.84 and 1.34 powers of monomer concentration in the presence and absence of lecithin, respectively. The calculated higher kinetic order, 1.84, with respect to monomer concentration can also be accounted for by the capture of MAn in the interior of the reversed lecithin micelles. Thus, when the monomer concentration is low, the proportion of the captured MAn against the free MAn can be high. The copolymerization activity of the captured MAn is considered to be depressed by the reversed lecithin micelle. Consequently, the kinetic order might be heightened.

Figure 5 also shows that the intrinsic viscosity of the copolymer increases with an increase in the rate of copolymerization as a result of increasing monomer concentration.

The specific rotation of the copolymer was increased with a decrease in monomer concentration. However, the specific rotation of the copolymer was decreased by further decreasing the monomer concentration. The decrease in specific rotation indicates that the copolymerization proceeds in the exterior of the reversed lecithin micelle, unaffected by the polar head group of lecithin under these conditions.

Influence of Polymerization Temperature. The influence of temperature on the copolymerization was examined in the range of 40 to 80 °C, in the presence and absence of

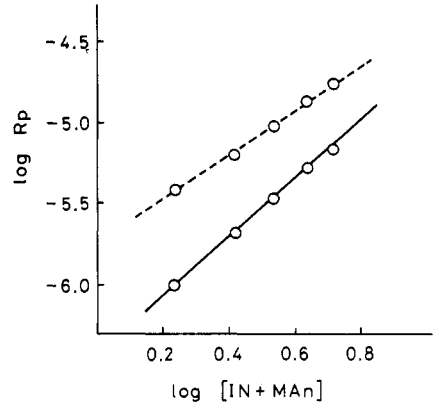

Figure 5. Relationships between log *Rp* and log [IN + MAn] for the copolymerization. [IN] = [MAn] and [AIBN] = 1.0×10^{-3} mol L^{-1}. (-○-) [lecithin] = 6.41×10^{-2} mol L^{-1}; (-○-) [lecithin] = 0.

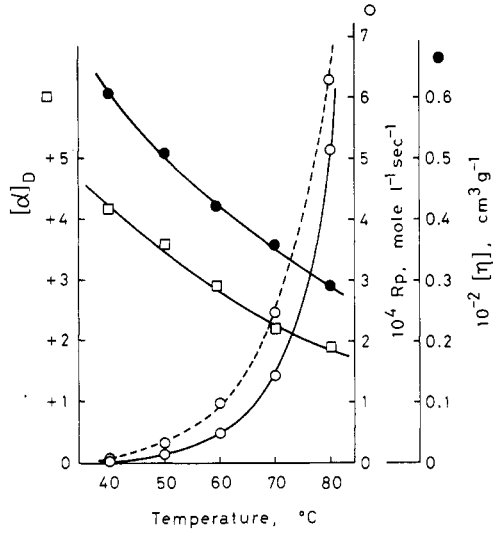

Figure 6. Influence of temperature on the rate of copolymerization (○), intrinsic viscosity (●), and specific rotation (□) of the copolymer. [IN] = [MAn] = 1.724 mol L^{-1}, [AIBN] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene. (-○-) In the absence of lecithin.

lecithin. The results of the copolymerization are illustrated graphically in Figure 6.

The rate of copolymerization was enhanced considerably by increasing polymerization temperature in the presence and absence of lecithin. The apparent activation energy for the copolymerization was calculated from Arrhenius plots as 27.3 kcal mol^{-1} in the presence of lecithin and 22.9 kcal mol^{-1} in the absence of it. It is clear from Figure 6 that the absolute value of the rate of copolymerization was lower in the presence of lecithin than that in its absence at every polymerization temperature and that the rate of copolymerization was appreciably depressed by lecithin at a lower temperature. This behavior may result from the difference in intensity of the electrostatic interaction between MAn and lecithin at different temperatures. Thus, the interaction is considered to be weaker at a higher temperature than that at a lower one. This prediction was also supported by the optical data for the copolymers. As can be seen from Figure 6, the specific rotation of the copolymer decreased significantly with an increase in polymerization temperature. This result is of interest in connection with thermal transitions[11–13] of the lecithin micelle. Disorder of hydrocarbon chains of lecithin seems reasonable as an interpretation of the decrease in specific rotation of the copolymer. In other words, the interaction between

MAn and lecithin micelle is thought to be weakened by the disorder of lecithin micelle caused by an increase in temperature.

Conclusion

The copolymerization of IN with MAn gave an alternating copolymer in the presence and absence of lecithin. The chiral surface active (amphiphilic) substance, lecithin, lowered the rate of copolymerization and intrinsic viscosity of the copolymer. The influences of lecithin on the copolymerization are considered to be due to an electrostatic interaction between MAn and the polar head group of lecithin. In nonpolar solvents such as benzene, lecithin molecules associate to form reversed micelles. The nonpolar monomer, IN, may exist at the exterior of the reversed lecithin micelle, while the polar monomer, MAn, may be captured within the micelles, in which an electrostatic interaction between MAn and lecithin can be present. The asymmetric induction copolymerization of IN with MAn is considered to be caused by the electrostatic interaction between MAn and the polar head group of the chiral amphiphilic substance, lecithin. The copolymerization may proceed via CT complex of IN and MAn affected by the lecithin micelle. The asymmetry is thought to be induced at the site of the MAn monomer units in the backbone of the copolymer. The λ_0 values of the copolymers supported this assumption.

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Notes

Observation of Cis Residues in Poly(γ-hydroxy-L-proline) in Aqueous Solution

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It has recently been established, by means of high-field (270 MHz) proton Fourier-transform NMR, that poly(L-proline) in D_2O at room temperature has about 2–3% of its imide bonds in the cis configuration.[1] As Schimmel and Flory[2] pointed out and as has been further discussed more recently[3] the presence of only a very small fraction of cis residues will markedly decrease the chain dimensions and average properties associated with the molecule and thus requires a reexamination of the published conformational energy maps. In a recent comprehensive report it has been shown that the average dimensional properties of poly(γ-hydroxyl-L-proline)[4] are very similar to those of poly(L-proline). The characteristic ratios of the two polymers in H_2O at 30 °C are 15.9 ± 1.6[4] and 13.7 ± 0.9,[5] respectively.

With the statistical conformation of the two polymers now shown to be similar, by experiment, the question as to whether cis imide groups are also present in poly(γ-hydroxyl-L-proline) becomes a matter of obvious importance. Unfortunately, proton NMR is not suitable for this purpose since the spectral region anticipated for the cis imide bond is obscured by the C^γ–H resonance in aqueous solution.[6] However, the utilization of ^{13}C NMR has shown potential for this purpose, despite the disadvantage of requiring much larger quantities of material. It has been successful in detecting cis peptide bonds in the copolymers poly(L-prolylglycyl) and poly(γ-hydroxyl-L-prolylglycyl).[7]

In the present work we wish to report the detection of a small percentage of cis imide bonds in poly(γ-hydroxyl-L-proline) in D_2O using high-field (67.9 MHz) ^{13}C Fourier-transform NMR. To establish the validity of the method we have also examined the corresponding spectrum of poly(L-proline) in D_2O at 30 °C. The pertinent region of the spectrum of this polymer is given in Figure 1. The delay times used to obtain the spectra were chosen in accord with the spin–lattice relaxation times, T_1, reported by Torchia and Lyerla.[7] Thus saturation of resonances is avoided. The assignment of the resonances is based on the previous work by Dorman et al.[8] The resonances assigned to the C^γ and C^β in the cis configuration can be clearly observed. Two small resonances appear downfield from the C^β trans. The resonance furthest downfield (ca. 30.6 ppm) is assigned to the cis C^β in accord with previous results for poly(L-proline). The other minor resonance that is observed cannot be definitely assigned but may be due to sequential effects of the cis isomer or another trans conformer. The integrated areas of each of these cis resonances are 2–3% of the corresponding trans resonance. Thus we have obtained essentially the same results as reported using ^1H NMR[1] indicating that the nuclear Overhauser enhancements are comparable for each of the two carbons in the cis and trans configuration.

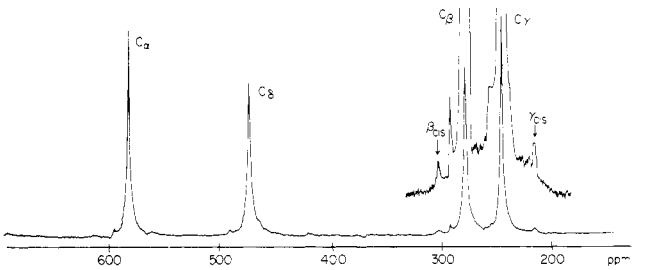

Figure 1. Partial carbon-13 Fourier-transform NMR spectrum at 67.9 MHz of poly(L-proline) (M = 9000) in D_2O at room temperature, 20 500 scans, 6.1 h total time. All spectra were obtained using a 4000 Hz total spectral width (8192 frequency domain points), a pulse repetition rate of 1.074 s, and an artificial broadening of 3 Hz due to exponential filtering to enhance sensitivity. Chemical shift scale is in ppm from Me_4Si. Arrows indicate cis resonance assignments.

With this confirmation, by means of carbon-13 spectroscopy, of the previous conclusions for poly(L-proline) similar

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