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

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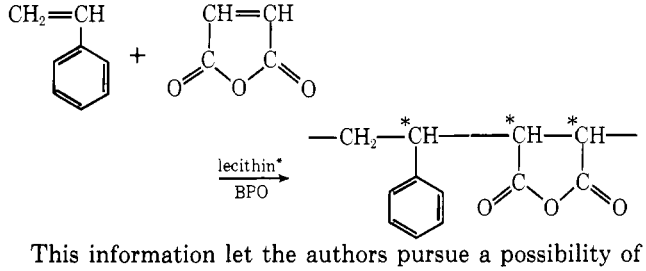
ABSTRACT: The copolymerization of styrene (St) with maleic anhydride (MAn) was carried out in the presence of a chiral surface active substance, lecithin, using benzoyl peroxide (BPO) in benzene. It was found that lecithin affects the rate of copolymerization and molecular weight of the resulting copolymer. These influences of lecithin were confirmed to be attributed not to a chain-transfer reaction to lecithin molecules but to an electrostatic interaction between MAn and reversed lecithin micelle. Moreover, the copolymer obtained in the presence of lecithin was observed to be optically active. The observed optical activity was considered to be due to an excess of one configuration in the chain backbone induced by the chirality of lecithin during the propagation step of the copolymerization.

In the numerous studies on asymmetric organic reactions,[1] there are not so many examples of asymmetric syntheses using asymmetric fields such as chiral media, matrices, crown ethers, etc.

In the previous papers,[2,3] the authors revealed that the optically active and zwitterionic surface active substance, lecithin, acts as an asymmetric inducing agent in the oil/water interfacial emulsion systems. Thus, in the presence of lecithin, the reduction of some unsymmetric and water-insoluble ketones such as acetophenone with an aqueous $NaBH_4$ solution caused optically active carbinols.[2] An asymmetric induction was also achieved by the oil/water interfacial emulsion copolymerization of styrene with maleic acid in the presence of lecithin.[3] From the results, it was concluded that the lecithin micelle is considered to be an asymmetric field and that the heterophase reaction and copolymerization were allowed to proceed mainly in the vicinity of the micell–water interface, in which the stereochemical controls were brought about by the chirality of lecithin, which has an asymmetric carbon atom at the 2 position of the glycerine moiety.

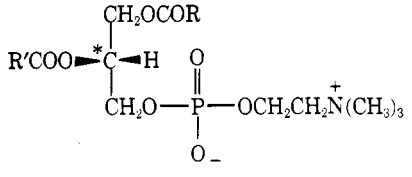
Micellization of lecithin was investigated[4-9] in various solvents of different dielectric constants. Large micelles are present in water, having the normal structure with hydrocarbon chains in the interior.[10,11] In nonpolar solvents such as benzene, however, reversed micelles are formed in which the polar head groups of lecithin constitute the micellar interior.



This information let the authors pursue a possibility of asymmetric induction by copolymerization of a vinyl monomer with an α,β-disubstituted olefin in the presence of lecithin in an organic solvent. That is, this paper describes the asymmetric induction copolymerization of styrene with maleic anhydride by the chiral surface active substance, lecithin.

Experimental Section

Materials. Lecithin (from soy beans) was supplied by the Katayama Chemical Co. Ltd. and used without further purification. The structure of soy bean lecithin is shown as follows:



R and R′ are long acyl groups such as stearic, oleic, linoleic, linolenic, etc. The average number of molecular weight of lecithin is about 780: $[\alpha]_D$ +8.71° (*c* 2.40, THF). Commercially available maleic anhydride (MAn) was purified by recrystallization from water-free chloroform. Styrene (St) and other monomers were purified by the usual methods and distilled under reduced pressure in a stream of nitrogen before use. Benzoyl peroxide (BPO) was purified by recrystallization from a chloroform solution with a large quantity of methanol. Benzene and other organic solvents were purified by the conventional methods before use.

Polymerization Procedure. Copolymerization of St with MAn was carried out in a sealed tube, using BPO as an initiator. The prescribed amounts of St, MAn, BPO, 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 the definite time of polymerization, the tube was cooled in a dry ice/methanol bath in order to stop the polymerization. After tapping the tube, the contents were added to a 1:2 mixture of benzene and *n*-hexane. The precipitated copolymer was filtered, dried in vacuo, and purified by reprecipitation from a THF solution with a large quantity of *n*-hexane three to five times and subjected to elemental analysis and physical measurements.

Physical Measurements. Intrinsic viscosity of the copolymers was measured in THF at 26 °C by using an UBBELOHDE type viscometer. The average number of the molecular weight of the alternating copolymers was calculated using the following equation of Chow:[12]

$$[\eta] = 3.98 \times 10^{-4}\overline{M}_w^{0.596}$$

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.

Results and Discussion

Copolymerizations of Various Monomers with Maleic Anhydride in the Presence of Lecithin. Several kinds of monomers were copolymerized with maleic anhydride (MAn) in the presence of lecithin, using benzoyl peroxide (BPO) as an initiator. The conditions and results of the copolymerizations are summarized in Table I.

As shown in Table I, the copolymerizations of styrene (St), α-methylstyrene (α-MeSt), indene (IN), and 1,3-pentadiene (PD) with MAn gave corresponding alternating copolymers. The copolymers of St with MAn, α-MeSt with MAn, and IN with MAn were observed to be optically active, whereas optical activity was not observed for the copolymer of PD with MAn. The copolymerization of methyl methacrylate (MMA) with MAn gave a slightly optically active copolymer rich in MMA units. Mixing of isoprene (IP) and MAn caused an exothermic reaction, which may be a Diels-Alder reaction, and copolymerization rarely proceeded. In the system of *n*-butyl vinyl ether (BVE)/MAn in the presence of lecithin, the mixture became brown to black and no polymer was obtained.

In the above copolymerizations, the optical activity observed is considered to be due to asymmetry induced to the backbone of the copolymer chain by the chirality of lecithin.

Table I
Copolymerizations of Various Monomers (M_1) with Maleic Anhydride (M_2) in the Presence of Lecithin[a,d]

M_1, mol L^{-1}	M_2, mol L^{-1}	[BPO], mol L^{-1}	Polymn. Time, h	Yield of polymer, g	$[m_1]/([m_1]+[m_2])$[b]	$[\alpha]_D$[c]	λ_0, nm
St, 1.73	MAn, 1.73	1.0×10^{-3}	12	0.326	0.48	+7.23	205
α-MeSt, 1.55	MAn, 1.73	1.0×10^{-2}	30	0.508	0.46	+2.27	203
MMA, 1.87	MAn, 1.73	1.0×10^{-2}	30	0.984	0.62	+0.36	
IN, 1.72	MAn, 1.73	1.0×10^{-2}	18	0.615	0.47	+4.67	206
PD, 2.00	MAn, 1.73	1.0×10^{-2}	30	0.685	0.49	0.00	
IP, 2.00	MAn, 1.73	1.0×10^{-2}	30	trace			
BVE, 1.56	MAn, 1.73	1.0×10^{-2}	30	0.00			

[a] [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene. Total volume, 10 mL. Polymerization temperature, 40 °C. [b] Determined by elemental analysis. [c] Measured in THF at 25 °C. [d] St = styrene; α-MeSt = α-methylstyrene; MMA = methyl methacrylate; IN = indene; PD = 1,3-pentadiene; IP = isoprene, BVE = *n*-butyl vinyl ether; MAn = maleic anhydride.

Table II
Influence of Lecithin on the Copolymerization of Styrene (St) with Maleic Anhydride (MAn)[a]

Run	Lecithin, g (mol L^{-1})	Polym time, h	Yield of polymer, g	$10^6 R_p$, mol L^{-1} s^{-1}	$10^{-2}[\eta]$[b] cm^3 g^{-1}	$10^{-6}\overline{M}_w$[c]	$[\alpha]_D$[d]
L-1	0	6	0.574				0.00
L-2		12	1.257	28.8	3.36	3.88	0.00
L-3		18	1.715				0.00
L-4	1.95×10^{-3} (2.50×10^{-4})	6	0.550				0.00
L-5		12	1.326	30.4	3.39	3.94	0.00
L-6		18	1.932				0.00
L-7	3.91×10^{-3} (5.01×10^{-4})	6	0.628				0.00
L-8		12	1.354	31.0	3.62	4.40	0.00
L-9		18	1.855				0.00
L-10	7.81×10^{-3} (1.00×10^{-3})	6	0.401				+0.02
L-11		12	1.190	27.3	3.90	4.98	+0.02
L-12		18	1.817				+0.02
L-13	1.56×10^{-2} (2.00×10^{-3})	6	0.360				+0.22
L-14		12	0.919	21.0	3.76	4.69	+0.20
L-15		18	1.547				+0.20
L-16	3.13×10^{-2} (4.01×10^{-3})	6	0.265				+0.56
L-17		12	0.672	15.4	3.46	4.07	+0.53
L-18		18	1.132				+0.50
L-19	6.25×10^{-2} (8.01×10^{-3})	6	0.243				+1.67
L-20		12	0.477	10.9	3.28	3.72	+1.67
L-21		18	0.736				+1.56
L-22	0.125 (1.60×10^{-2})	6	0.235				+3.10
L-23		12	0.426	9.8	3.24	3.65	+3.00
L-24		18	0.676				+2.65
L-25	0.250 (3.21×10^{-2})	6	0.209				+6.33
L-26		12	0.322	8.4	3.12	3.42	+5.72
L-27		18	0.574				+4.60
L-28	0.500 (6.41×10^{-2})	6	0.183				+8.00
L-29		12	0.337	7.7	3.03	3.26	+7.33
L-30		18	0.539				+7.20
L-31	1.000 (0.128)	6	0.184				+6.00
L-32		12	0.367	7.3	2.75	2.77	+5.60
L-33		18	0.466				+5.60
L-34	2.000 (0.256)	6	0.167				+3.50
L-35		12	0.291	6.7	2.57	2.47	+3.00
L-36		18	0.393				+3.25

[a] [St] = [MAn] = 1.73 mol L^{-1} and [BPO] = 1.0×10^{-1} in benzene. Total volume, 10 mL. Polymerization temperature, 40 °C. [b] Measured in THF at 26 °C. [c] Calculated using the equation of Chow (cf. ref 12). [d] Measured in THF at 25 °C.

Table III
Homopolymerization of Styrene in the Presence and Absence of Lecithin[a]

Run	Lecithin, g (mol L^{-1})	Polymn. time, h	Yield of polymer, g	$10^6 R_p$, mol L^{-1} s^{-1}	$10^{-2}[\eta]$,[b] cm^3 g^{-1}	$10^{-5}\overline{M}_w$[c]
H-1	0	36	0.458			
H-2		60	0.724	3.2	0.67	1.48
H-3		84	0.954			
H-4	0.016 (2.0×10^{-3})	36	0.477			
H-5		60	0.736	3.2	0.68	1.51
H-6		84	0.971			
H-7	0.063 (8.0×10^{-3})	36	0.434			
H-8		60	0.725	3.2	0.69	1.54
H-9		84	0.988			
H-10	0.250 (3.2×10^{-2})	36	0.418			
H-11		60	0.745	3.2	0.68	1.51
H-12		84	0.979			

[a] [St] = 4.33 mol L^{-1} and [BPO] = 2.0×10^{-2} mol L^{-1} in benzene. Total volume, 10 mL. Polymerization temperature, 40 °C. [b] Measured in benzene at 30 °C. [c] Calculated using the following equation of Krigbaum and Flory (cf. ref 18); $[\eta] = 9.52 \times 10^{-5}\overline{M}_n^{0.744}$.

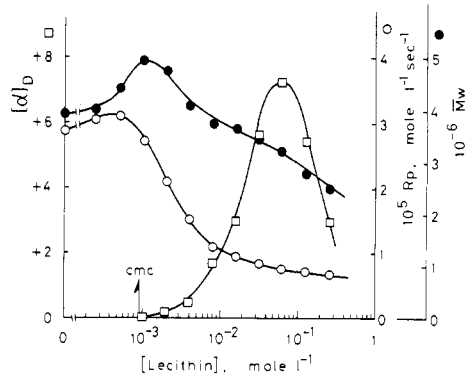


Figure 1. Influence of lecithin on the rate of copolymerization (○), molecular weight (●), and specific rotation (□) of the copolymer. [St] = [MAn] = 1.73 mol L^{-1} and [BPO] = 1.0×10^{-3} mol L^{-1} in benzene. Temperature, 40 °C; time, 12 h.

For the purpose of obtaining more fully detailed information on the asymmetric induction copolymerization by the chiral surface active substance, lecithin, St was copolymerized with MAn under various conditions in the subsequent experiments.

Influence of Lecithin Concentration. The copolymerization of a constant amount of St with equimolar MAn was carried out in benzene in the presence of various amounts of lecithin. The detailed descriptions of the conditions and results of the copolymerization are given in Table II and illustrated graphically as a function of lecithin concentration in Figure 1.

The infrared spectra of the copolymers obtained had the same shape as those obtained from the system in the absence of lecithin. The rate of copolymerization was observed to be maximized as a result of addition of a proper amount of lecithin to the copolymerization system. This point of lecithin concentration, 5.01×10^{-4} mol L^{-1}, that is 0.039 w/v %, is close to the value of critical micelle concentration (cmc) for the formation of solubilizing lecithin aggregates in benzene. Small micelles appear even at very low concentrations,[4] and there is a cmc (0.073%)[5] at which aggregation of small into large micelles begins.

Figure 1 shows that the further addition of lecithin to the copolymerization system lowers the rate of copolymerization. The molecular weight of the resulting copolymer was also observed to be variable with the lecithin concentration in a similar tendency as the rate of copolymerization. These influences of lecithin on the rate of copolymerization and molecular weight of the copolymer are of interest in connection with those observed for the interfacial emulsion copolymerization of styrene with maleic acid.[3] For the purpose of elucidation of the nature of the retardation effect of lecithin on the rate of copolymerization of St with MAn, homopolymerization of St was carried out in the presence and absence of lecithin in benzene.

As can be seen from the results in Table III, lecithin did not exert any influence on the polymerization of St. Thus, there is no thinking of an occurrence of chain-transfer reaction to lecithin molecules in radical polymerizations. The observed retardation effect on the rate of copolymerization may be attributed to a certain inhibition of formation of charge-transfer (CT) complex of St with MAn by an electrostatic interaction between MAn and the polar head group of lecithin.

Now, assuming that the micelle built up with chiral lecithin molecules is considered to be an asymmetric field, the asymmetric induction copolymerization must be possible merely beyond the cmc value in lecithin concentration. The results in Table II and Figure 1 are compatible with the above prediction. The optical rotation of the resulting copolymer began to be detectable at about the cmc value and increased to maximum point with an increase in lecithin concentration in the copolymerization system. It is thought that the situation of lecithin micelle at about 6.3×10^{-2} mol L^{-1} is suitable for the asymmetric induction copolymerization. However, there is no clear explanation for the decrease in specific rotation of the copolymer obtained from the system in lecithin concentration higher than 0.1 mol L^{-1}.

The optical rotatory dispersion (ORD) measurements for the copolymers gave positive plain curves. From the corresponding ORD curves, the λ_0 values of the copolymers were calculated to be 200 to 210 nm, by use of the simple Drude equation.[13] The λ_0 values calculated are close to the λ_{max} of the UV absorption band of the carbonyl group, 212 nm.

Influence of Variation in Monomer Ratio. The copolymerization of St with MAn was carried out in the presence of a constant amount of lecithin. The molar concentration of the total monomer was kept constant. The detailed descriptions of the conditions and results of the copolymerization are shown in Table IV and illustrated graphically in Figure 2.

It is clear from Table IV and Figure 2 that the copolymer composition is independent of St/MAn composition in mo-

Table IV
Influence of Monomer Ratio on the Copolymerization of Styrene (St, M_1) with Maleic Anhydride (MAn, M_2)[a]

Run	[St], mol L^{-1}	[MAn], mol L^{-1}	Polymn. time, h	Yield of polymer, g	$10^6 R_p$, mol L^{-1} s^{-1}	$[m_1]/([m_1]+[m_2])$[b]	$10^{-2}[\eta]$,[c] cm^3 g^{-1}	$10^{-6}\bar{M}_w$[d]	$[\alpha]D$[e]
F-1	0.434	3.036	12	0.138					
F-2			18	0.232	3.36	0.47	2.41	2.22	+7.67
F-3			24	0.289					
F-4	0.867	2.603	12	0.271					
F-5			18	0.481	6.60	0.49	3.80	4.76	+7.20
F-6			24	0.571					
F-7	1.301	2.169	12	0.396					
F-8			18	0.534	8.22	0.49	3.97	5.12	+7.67
F-9			24	0.657					
F-10	1.735	1.735	12	0.296					
F-11			18	0.514	7.06	0.49	3.03	3.26	+7.33
F-12			24	0.589					
F-13	2.169	1.301	12	0.178					
F-14			18	0.281	4.40	0.48	2.08	1.73	+8.00
F-15			24	0.390					
F-16	2.603	0.867	12	0.080					
F-17			18	0.163	2.43	0.49	1.20	0.69	+9.33
F-18			24	0.213					
F-19	3.036	0.434	12	0.024					
F-20			18	0.032	0.64	0.50			
F-21			24	0.054					

[a] [St] = [MAn] = 3.47 mol L^{-1}, [BPO] = 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. [b] Determined by elemental analysis. [c] Measured in THF at 26 °C. [d] Calculated using the equation of Chow (cf. ref 12). [e] Measured in THF at 25 °C.

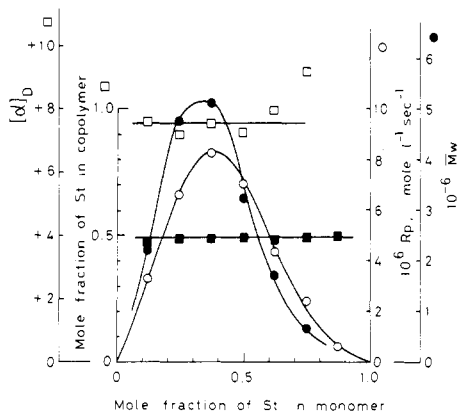


Figure 2. Influence of monomer ratio on the rate of copolymerization (○), molecular weight (●), mole fraction of St (■), and specific rotation (□) of the copolymer. [St] + [MAn] = 3.47 mol L^{-1}, [BPO] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene. Temperature, 40 °C; time, 18 h.

nomer feed and that every copolymer is alternating. This result indicates that the copolymerization proceeds via CT complex of St and MAn even in the presence of lecithin. Interestingly, the maximum point of the rate of copolymerization deviated from the equivalent concentration[14] of St and MAn in monomer feed. The deviation of the maximum point from 1:1 St/MAn monomer concentration to a lower concentration of St may be due to a "capture" of MAn within the reversed lecithin micelle. Consequently, the concentration of MAn effective for the copolymerization must be decreased by the reversed lecithin micelle. The maximum point of molecular weight of the resulting copolymer also deviated from the equivalent concentration of St and MAn in monomer feed as the rate of copolymerization.

The specific rotation of the copolymer is also plotted as a function of St mole fraction in monomer feed in Figure 2. The intensity of specific rotation of the copolymer was approximately constant regardless of St mole fraction in monomer feed. The approximately constant specific rotation of the resulting copolymers indicates that the MAn is almost captured within the reversed lecithin micelle and that the asymmetric induction copolymerization proceeds through the "asymmetric field" via CT complexes of St and MAn, which are separated into the exterior and interior of the lecithin micelle, respectively.

Influence of Monomer Concentration. Various concentrations of St were copolymerized with equimolar amounts of MAn in the presence of a constant amount of lecithin. The conditions and results of the copolymerization are summarized in Table V and illustrated graphically in Figure 3.

It is clear from Table V and Figure 3 that the degree of the influence of lecithin on the copolymerization is larger at a lower monomer concentration than that at a higher monomer concentration. In Figure 3, the rates of copolymerization, R_p, in the presence and absence of lecithin are plotted as a function of monomer concentration. It can be seen than the rates of the copolymerization increase exponentially with an increase in monomer concentration. As shown in Figure 4, the plots of log ([St] + [MAn]) vs. log R_p gave straight lines. From the slopes of these straight lines, the rate of copolymerization was found to be proportional to 2.33 and 1.48 powers of monomer concentration in the presence and absence of lecithin, respectively. The calculated higher kinetic order, 2.33, with respect to monomer concentration can also be accounted for by the capture of MAn in the interior of the reversed lecithin micelle. Thus, it is thought that the proportion of the captured MAn against the free MAn is higher at a lower monomer concentration than that at a higher monomer concentration and that the captured MAn is depressed to copolymerize by the reversed lecithin micelle. Consequently, the observed kinetic order might be hightened. Figure 3 also shows that the molecular weight of the copolymer increases and the specific rotation of the copolymer decreases with an increase in the rate of copolymerization as a result of increasing monomer concentration.

Influence of Temperature. The copolymerization of St with MAn was carried out in the range of 40 to 70 °C in the

Table V
Influence of Monomer Concentration on the Copolymerization of Styrene (St) with Maleic Anhydride (MAn)[a]

Run	[St], mol L^{-1}	[MAn], mol L^{-1}	Polymn. time, h	Yield of polymer, g	$10^6 R_p$, mol L^{-1} s^{-1}	$10^{-2}[\eta]$,[b] cm^3 g^{-1}	$10^{-6}\overline{M}_w$[c]	$[\alpha]_D$[d]
M-1	0.87	0.87	12	0.072		1.04	0.54	+10.67
M-2			18	0.115	1.8			+11.13
M-3			24	0.157				+10.67
M-4	1.30	1.30	12	0.171		2.23	1.95	+7.20
M-5			18	0.271	4.0			+6.00
M-6			24	0.372				+5.67
M-7	1.73	1.73	12	0.375		3.14	3.46	+5.34
M-8			18	0.535	8.5			+4.00
M-9			24	0.739				+3.30
M-10	2.17	2.17	12	0.627		3.76	4.69	+3.20
M-11			18	0.964	14.7			+2.56
M-12			24	1.319				+1.67
M-13	2.60	2.60	12	1.089		4.54	6.43	+1.60
M-14			18	1.431	24.0			+1.35
M-15			24	2.084				+1.02

[a] [St] = [MAn], [BPO] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 3.2×10^{-2} mol L^{-1} in benzene. Total volume, 10 mL. Polymerization temperature, 40 °C. [b] Measured in THF at 26 °C. [c] Calculated using the equation of Chow (cf. ref 12). [d] Measured in THF at 25 °C.

Table VI
Influence of Temperature on the Copolymerization of Styrene (St) with Maleic Anhydride (MAn)[a]

Run	Temp, °C	Polymn. time, h	Yield of polymer, g	R_p, mol L^{-1} s^{-1}	$10^{-2}[\eta]$,[b] cm^3 g^{-1}	$10^{-6}\overline{M}_w$[c]	$[\alpha]_D$[d]
T-1	40	18	0.235				+6.21
T-2		24	0.325	3.8×10^{-6}			+5.45
T-3		36	0.435		2.04	1.68	+5.34
T-4	50	3	0.137				+3.34
T-5		6	0.304	1.3×10^{-5}			+3.31
T-6		9	0.432		2.00	1.63	+2.81
T-7	60	2	0.367				+2.50
T-8		3	0.558	5.0×10^{-5}	2.22	1.94	+2.36
T-9		4	0.754				+2.19
T-10	70	0.75	0.388				+1.82
T-11		1	0.526	1.9×10^{-4}	2.40	2.21	+1.74
T-12		1.25	0.797				+1.73

[a] [St] = [MAn] = 1.30 mol L^{-1}, [BPO] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 3.2×10^{-2} mol L^{-1} in benzene. Total volume, 10 mL. [b] Measured in THF at 26 °C. [c] Calculated using the equation of Chow (cf. ref 12). [d] Measured in THF at 25 °C.

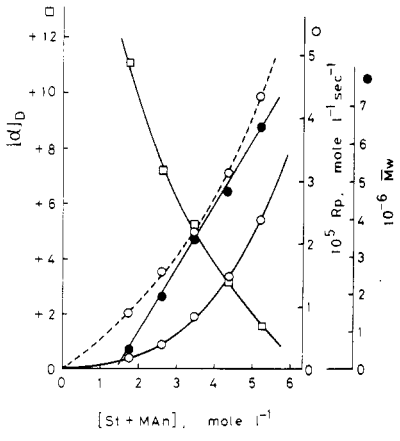


Figure 3. Influence of monomer concentration on the rate of copolymerization (○), molecular weight (●), and specific rotation (□) of the copolymer. [St] = [MAn], [BPO] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 3.2×10^{-2} mol L^{-1} in benzene. Temperature, 40 °C; time, 18 h. (--○--) in the absence of lecithin.

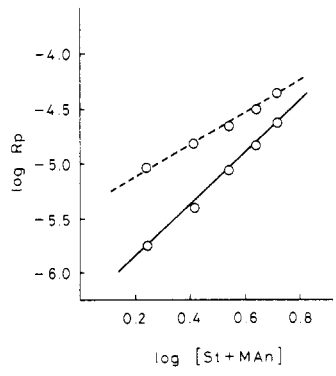


Figure 4. Relationships between log R_p and log [ST + MAn] for the copolymerization. [St] = [MAn] and [BPO] = 1.0×10^{-3} mol L^{-1}: (—) [lecithin] = 3.2×10^{-2} mol L^{-1}; (- - -) [lecithin] = 0.

presence and absence of lecithin. The conditions and results of the copolymerization are summarized in Table VI and shown graphically in Figure 5.

The rate of copolymerization was enhanced by an increasing in polymerization temperature in the presence and absence of lecithin. The overall activation energy for the copolymerization was calculated as 23.7 and 22.6 kcal mol^{-1} in the presence and absence of lecithin, respectively.

The specific rotation of the copolymer decreased with an increase in temperature of the copolymerization system. This result is of interest in connection with thermal transition[15-17] of lecithin micelle. Disorder of the hydrocarbon chain of lec-

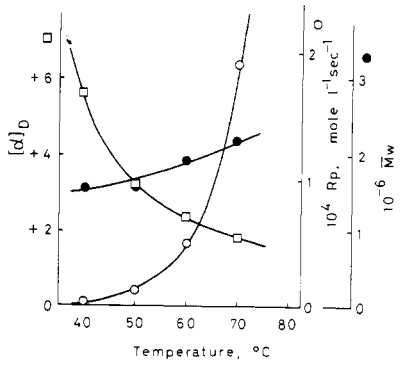


Figure 5. Influence of temperature on the rate of copolymerization (○), molecular weight (●), and specific rotation (□) of the copolymer. [St] = [MAn] = 1.30 mol L^{-1}, [BPO] = 1.0×10^{-3} mol L^{-1}, and [lecithin] = 3.2×10^{-2} mol L^{-1} in benzene.

ithin seems reasonable for an interpretation of the decrease in specific rotation of the copolymer. In other words, the interaction between MAn and lecithin micelle seems to be weakened by the disorder of lecithin micelle aggregates with an increase in temperature.

Mechanism of the Asymmetric Induction Copolymerization of St with MAn by Lecithin. St is a nonpolar monomer, whereas MAn is a polar monomer. Lecithin is an amphiphilic substance with a high lipophile property because of its two long hydrocarbon chains. In nonpolar solvents, such as benzene, reversed micelles are formed in which the polar head groups of lecithin molecules constitute the micellar interior. In the micellar solution, St exists in the exterior of the lecithin micelle, whereas MAn exists in the interior of it as shown schematically in Figure 6.

The asymmetric carbon atom is present near the polar head group of the lecithin molecule. Consequently, the MAn captured wihin the reversed lecithin micelle must be affected by the asymmetric carbon atom of lecithin. This assumption was supported by the fact that the specific rotation of lecithin is slightly increased by the addition of MAn as shown in Figure 7. On the other hand, St did not exert any effect on the specific rotation of lecithin.

These results indicate the presence of the electrostatic interaction between MAn and lecithin.

The asymmetric induction copolymerization is considered to proceed by the following two schemes: (a) copolymerization via CT complex of St and MAn unaffected by lecithin micelle (the sequence, –St·MAn–, is optically inactive)

$$\text{St} + \text{MAn} \rightleftharpoons [\text{St} \cdots \text{MAn}] \rightarrow \text{–St·MAn–}$$

(b) copolymerization via CT complex of St with MAn affected by lecithin micelle (the sequence, –St·MAn*–, is optically active)

$$\text{lecithin}^* + \text{MAn} \rightleftharpoons [\text{lecithin} \cdots \text{MAn}]^* \overset{\text{St}}{\rightleftharpoons}$$

$$[\text{St} \cdots \text{lecithin} \cdots \text{MAn}]^* \rightarrow \text{–St·MAn*–}$$

The asymmetry is thought to be induced to the side of MAn

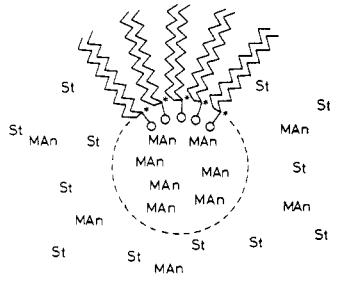


Figure 6. Schematic representation of a reversed lecithin micelle containing MAn.

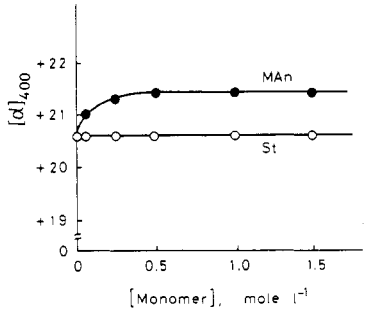


Figure 7. Variation in specific rotation of lecithin: [lecithin] = 3.1×10^{-2} mol L^{-1} (c 2.43, benzene); temperature, 25 °C.

monomer units of the chain backbone of the copolymer. λ_0 values (200 to 210 nm) of the optically active copolymers supported the above schemes.

At the present time, the authors are engaged in studying the asymmetric induction copolymerizations of other monomers in the presence of lecithin.

References and Notes

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