(41) The ^{13}C may be partially decoupled from the deuterons because of scalar relaxation of the second kind (A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961, pp 309–312).
(42) There are too many peaks for a simple dyad analysis and too few for tetrad effects. Configurational isomerism contributes only to a broadening or fine structuring of the peaks. Note also that the simple parity relationships which hold for configurational sequences in vinyl homopolymers and monomer sequences in vinyl copolymers (odd for α carbons and their substituents and even for β carbons) do not necessarily apply here.
(43) J. R. Ebdon and T. N. Huckerby, *Polymer*, **17**, 170 (1976).
(44) A sulfone group in the β position to a given carbon (e.g., the starred carbon in the sequence C*–C–SO_2) has two γ oxygens (i.e., those removed from the starred carbon by three bonds), which are responsible for the observed shielding of this carbon relative to its counterpart which has a carbon atom in the γ position. The spectra show that this shielding is approximately 4 ppm for methine carbons and 8 ppm for methylene carbons in poly(styrene sulfone)'s. This is demonstrated by the upfield positions of the carbon resonances in α(SMS), α(SMM), β(SMS), β(MMS) relative to those in the counterpart sequences, i.e., α(MMS), α(MMM), β(SMM), and β(MMM), respectively. An entirely analogous effect was observed in the ^{13}C spectra of poly(styrene peroxide)'s.[45] A γ shielding of 6.7 ppm by sulfone oxygens has recently been reported in the literature [G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108–114 (1976)].
(45) R. E. Cais and F. A. Bovey, *Macromolecules*, submitted.
(46) B. D. Coleman and T. G. Fox, *J. Polym. Sci., Part A*, **1**, 3183–3197 (1963).
(47) C. W. Pyun, *J. Polym. Sci., Part A-2*, **8**, 1111–1126 (1970).
(48) Sulfur dioxide (S) does not homopropagate; consequently, polysulfones prepared by free-radical copolymerization do not contain any sequences of successive placements of S.
(49) K. Matsuzaki, T. Uryu, T. Seki, K. Osada, and T. Kawamura, *Makromol. Chem.*, **176**, 3051–3064 (1975).
(50) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 889–899 (1975).
(51) The point at −78 °C was obtained from the literature datum $p(M) = 0.52$ for a polysulfone prepared from a 30 mol % styrene monomer mixture.[6] This polysulfone is insoluble in common NMR solvents and could not be examined in the present work. Nevertheless, the R value reported for this polymer indicates that $p(MMM) = 0$, hence $p(S) = p(MSM) = 0.48$, $p(MMS) = p(SMM) = 0.04$, and $p(SMS) = 0.44$, consequently $N_M(1) = 0.92$. It should be pointed out that the point obtained from the present results at 40 °C corresponds to a copolymer prepared from a 68 mol % styrene monomer mixture, which will have a different sequence distribution than a copolymer prepared at the same temperature but from a 30 mol % styrene monomer mixture (the points at 0 and −78 °C apply to polysulfones prepared from 30 mol % syrene mixtures). However, the macroscopic compositions of the polysulfones prepared at 40 °C are reported to vary little with monomer composition over the range 20 to 80 mol % styrene (cf. results at room temperature and 50 °C[6,29]), consequently the sequence distribution should also not depend to any large extent on the monomer composition in this range. These considerations do not alter the major conclusion drawn from the data.
(52) The labeling of the columns in Table I of ref 38 is incorrect. Using the author's notation, the column labeled T_{SO_2StSt} should read $T_{SO_2StSO_2}$, and that labeled $T_{StStSO_2} + T_{SO_2StSO_2}$ should read $T_{StStSO_2} + T_{SO_2StSt}$. The correct headings correspond to p(SMS) and p(MMS) + p(SMM), respectively, in the present notation.
(53) R. E. Cais and J. H. O'Donnell, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 263–272 (1976).
(54) Although all propagating sulfonyl radicals with a penultimate sulfone unit (i.e., ~SMS·) will be unstable above 40 °C in the presence of bulk monomer, their depropagation by the loss of sulfur dioxide may be prevented occasionally by the rapid addition of several styrene units, which effectively "lock in" the unstable sequence. Therefore a vanishingly small proportion of SMS sequences can be formed in copolymers prepared above 40 °C (e.g., note the very weak peaks at 64 and 49 ppm in Figure 3).
(55) These steps do not become significantly reversible until the temperature approaches 300 °C, the T_c for the homopolymerization of bulk styrene.[19]
(56) M. Izu and K. F. O'Driscoll, *J. Polym. Sci., Part A-1*, **8**, 1675–1685 (1970).
(57) R. E. Cais and J. H. O'Donnell, manuscript in preparation.

Asymmetric Induction by Interfacial Emulsion Copolymerization of Styrene with Maleic Acid in the Presence of Lecithin

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ABSTRACT: The copolymerization of styrene (St) with maleic acid (MAc) was carried out in the oil/water interfacial system at 40 °C, using potassium persulfate (KPS) as an initiator in a sealed tube. The addition of lecithin, which is a naturally occurring zwitterionic surface active and optically active substance, to this interfacial copolymerization system resulted in a water in oil type emulsification of the system and substantial changes in the rate of copolymerization. The copolymers obtained from the emulsion system were richer in styrene monomer units than those obtained from tetrahydrofuran (THF) solution system. Furthermore the copolymers obtained from the emulsion system were confirmed to be optically active. From the experimental results, it was concluded that polymer chains are forced to grow in the vicinity of oil/water interface in the copolymerization of St with MAc in the above system. The observed optical rotation indicates that an excess of one configuration in chain backbone was induced by the chirality of lecithin during the propagation step of the copolymerization. This process of asymmetric induction polymerization is regarded as an example of enantioface differentiating reaction using an asymmetric field built up with lecithin micelle.

Many studies on the asymmetric induction polymerizations of vinyl monomers have been undertaken for obtaining information on the mechanism of the polymerization. As the first attempt, optically active diamyl itaconate was polymerized by Walden[1] with a view to changing in optical rotation but the conception ended in failure. Marvel and his coworkers[2] undertook to induce asymmetry in the polymerization of styrene, methyl methacrylate, and acrylonitrile by the use of chiral radical initiators. However, no optical activity was detected in the resulting polymers. Marvel[3] and Overberger[4] polymerized optically active vinyl monomers, but no optical activity remained after removal of their original asymmetric groups.

Copolymerization with α,β-disubstituted olefin such as maleic anhydride overcomes the problem of pseudoasymmetry in homopolymerization of vinyl monomers. Schuerch et al. reported successful asymmetric polymer syntheses: that is, l-α-methylbenzyl methacrylate/maleic anhydride[5] and l-α-methylbenzyl vinyl ether/maleic anhydride[6] systems. These copolymers were optically active even after removal of their l-α-methylbenzyl group. The authors revealed that asymmetric induction can be also effected by alternating copolymerization of optically active α,β-disubstituted olefins with optically inactive vinyl monomers: that is, *N-endo*-bornyl maleimide/styrene,[7] N-l-menthyl malemide/styrene,[8] and N-l-menthyl maleimide/methyl methacrylate[8] systems.

Table I
Interfacial Copolymerization of Lipophilic Monomers (M_1) with Hydrophilic Monomers (M_2) in the Presence of Lecithin [a,f]

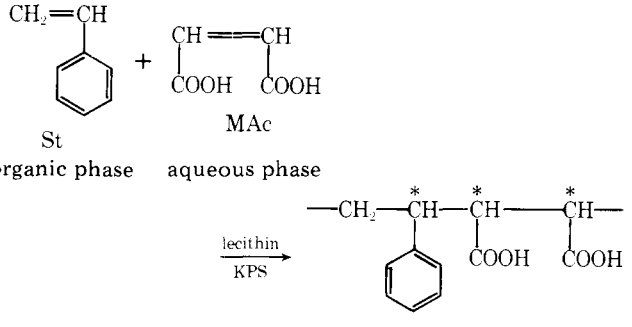
Organic phase (5 ml),[b] M_1, mol L^{-1}	Aqueous phase (10 ml),[c] M_2, mol L^{-1}	Polymn time, h	Yield of polymer, g	$[m_2]/([m_1]+[m_2])$[d]	$[\alpha]_{350}$[e]
St, 8.67	AAc, 4.40	2	1.28	0.65	0.00
St, 8,67	MAc, 3.40	8	0.65	0.24	+0.87
α-MeSt, 7.74	MAc, 3.40	96	0.00		
IN, 8.59	MAc, 3.40	96	0.00		
BVE, 7.73	MAc, 3.40	96	0.00		
MMA, 9.40	MAc, 3.40	10	1.17	0.02	0.00
PD, 10.03	MAc, 3.40	4	1.45	0.42	0.00
IP, 9.99	MAc, 3.40	4	1.35 (gel)		

[a] Polymerized in a sealed tube at 40 °C. Lecithin: 0.8 g (1.02×10^{-3} mol). [KPS] = 0.11 mol L^{-1} in aqueous phase. [b] 5 ml of lipophilic monomer. [c] 10 ml of aqueous solution. [d] Determined by elemental analysis. [e] Measured in THF at 25 °C. [f] St = styrene; α-MeSt = α-methylstyrene; IN = indene; BVE = n-butyl vinyl ether; MMA = methyl methacrylate; PD = 1,3-pentadiene; IP = isoprene; AAc = acrylic acid; MAc = maleic acid.

Alternatively, it seems possible to attain an asymmetric induction polymerization of vinyl monomer with α,β-disubstituted olefin, using an "asymmetric field". Lecithin is a naturally occurring zwitterionic surface active and optically active substance, so the lecithin micelle is considered to be an "asymmetric field".

Previously, the authors clarified the asymmetric reduction of unsymmetric water-insoluble ketones such as acetophenone and valerophenone with an aqueous $NaBH_4$ solution in the presence of lecithin.[9]

It must be also possible to use lecithin as a chiral catalyst (or field) for an asymmetric induction polymerization. An interesting example is presented here in which styrene (St) was copolymerized with maleic acid (MAc) in the oil/water



interfacial emulsion system in the presence of lecithin.

It was proved that lecithin functions as an asymmetric inducing reagent with the ability to change the apparent monomer reactivities during the copolymerization in the interfacial system.

Experimental Section

Materials. Styrene (St) was purified by the usual method and distilled under reduced pressure in a stream of nitrogen before use. Commercially available maleic acid (MAc) was used for the polymerization without further purification. Other commercially available monomers, viz., acrylic acid (AAc), α-methylstyrene (α-MeSt), indene (IN), n-butyl vinyl ether (BVE), methyl methacrylate (MMA), 1,3-pentadiene (PD), and isoprene (IP), were purified by the usual method and distilled before use.

Potassium persulfate (KPS) was purified by recrystallization from water. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Benzoyl peroxide (BPO) was purified by recrystallization from chloroform.

Lecithin (from soy beans) was supplied from the Katayama Chemical Co., Ltd., and used for the experiments without further purification. $[\alpha]_D^{22} + 7.84°$ (c 1.00, THF). Water, methanol, n-hexane, benzene, chloroform, and tetrahydrofuran (THF) were purified with the usual methods.

Polymerization Procedure. Interfacial Emulsion Copolymerization. All the polymerizations were carried out in sealed tubes, using KPS, AIBN, or BPO as initiators. The prescribed amounts of St, lecithin, benzene, initiator, MAc, and water were mixed to be emulsifed in a glass tube. The tube was flushed three times with nitrogen, sealed in vacuo, and shaken in an incubator at 40 °C. After the prescribed time of polymerization, the contents were added to twice the amount of THF in order to break the emulsification and then poured into a large excess of n-hexane to isolate the polymer. The resulting polymer was washed with water to remove MAc monomer and dried in vacuo. All the polymers were purified by reprecipitation from THF solution with n-hexane at least five times. The polymers were obtained as white polymer.

Solution Copolymerization. Solution copolymerization was carried out in tetrahydrofuran (THF) in a sealed tube, using AIBN as an initiator. After the polymerization the contents were poured into n-hexane to precipitate the polymer. The polymer was washed with water and dried in vacuo. Reprecipitation of the polymer was performed from THF solution with n-hexane.

Physical Measurements. Intrinsic viscosity of the polymers was measured in THF at 30 °C by using an UBBELOHDE type of viscometer. D-line optical rotation and optical rotatory dispersion measurements were carried out with a Jasco Model J-20 automatic recording spectropolarimeter equipped with a xenon source. IR spectra of copolymers were obtained on a Jasco Model IRA-2 Grating IR spectrometer.

Results and Discussion

Copolymerization of Lipophilic Monomers with Hydrophilic Monomers in the Interfacial System in the Presence of Lecithin. Lipophilic monomers such as styrene (St), indene (IN), methyl methacrylate (MMA), etc., were copolymerized with hydrophilic monomers, acrylic acid (AAc) and maleic acid (MAc), using KPS as an initiator in the oil/water interfacial emulsion system in the presence of lecithin. The conditions and results of the copolymerization were summarized in Table I.

An optically active polymer was obtained from the copolymerization of St with MAc, whereas the copolymer of St with AAc was confirmed to be optically inactive. This result proved that copolymerization of vinyl monomers with other vinyl monomers cannot overcome the problem of pseudoasymmetry in the polymer chain.

Other lipophilic monomers, α-methylstyrene (α-MeSt), indene (IN), n-butyl vinyl ether (BVE), methyl metacrylate (MMA), 1,3-pentadiene (PD), isoprene (IP), were copolymerized with MAc in the same manner as above. No polymer was obtained from the systems α-MeSt/MAc, IN/MAc, and BVE/MAc. Copolymerization of MMA with MAc and PD with MAc gave corresponding copolymer with no optical activity. The copolymer of IP with MAc was cross-linked and insoluble in any organic solvent.

From the above results, the copolymerization of St with

Table II
Interfacial Emulsion Copolymerization of Styrene (M_1) with Maleic Acid (M_2) Initiated by Radical Initiators [a]

Run No.	Initiator, mol ($mol\ L^{-1}$)	Yield of polymer, g	$[m_2]/([m_1]+[m_2])$ [b]	$10^{-2}[\eta]$, [c] $cm^3\ g^{-1}$	$[\alpha]_{350}$ [d]	Solubility in Benzene	THF	Water
1	AIBN, 1.1×10^{-3} (0.22 in organic phase)	0.306	0.08	0.26	+0.30	Sol.	Sol.	Insol.
2	BPO, 1.1×10^{-3} (0.22 in organic phase)	0.140	0.07	0.24	+0.32	Sol.	Sol.	Insol.
3	KPS, 1.1×10^{-3} (0.11 in aqueous phase)	0.311	0.32	0.27	+1.60	Swelling	Sol.	Insol.

[a] Polymerized in a sealed tube at 40 °C for 8 h. Organic phase (5 ml): [St] = 5.20 mol L^{-1} in benzene. Aqueous phase (10 ml): [MAc] = 3.40 mol L^{-1}. Lecithin: 0.8 g (1.02×10^{-3} mol). [b] Determined by elemental analysis. [c] Measured in THF at 30 °C. [d] Measured in THF at 25 ° C.

Table III
Influence of Lecithin on the Interfacial Emulsion Copolymerization of Styrene (M_1) with Maleic Acid (M_2) at 40 °C

Run No.	Lecithin, g	Organic phase [a] (5 ml) Styrene, mol L^{-1}	Aqueous phase [b] (10 ml) Maleic acid, mol L^{-1}	Aqueous phase [b] (10 ml) KPS, mol L^{-1}	Polymn time, h	Yield of polymer, g	$10^3\ Rp$, g L^{-1} s^{-1}	$[m_2]/([m_1]+[m_2])$ [c]	$10^{-2}[\eta]$, [d] $cm^3\ g^{-1}$	$[\alpha]_{350}$ [e]
L-1	0.0	8.67	3.40	0.11	4	0.557				0.00
L-2					8	1.084	2.50	0.52	0.54	0.00
L-3					12	1.627				0.00
L-4	0.2	8.67	3.40	0.11	4	0.627				+0.15
L-5					8	1.173	2.83	0.33	0.76	+0.15
L-6					12	1.874				+0.12
L-7	0.4	8.67	3.40	0.11	4	0.384				+0.59
L-8					8	0.702	1.89	0.27	0.57	+0.50
L-9					12	1.269				+0.50
L-10	0.8	8.67	3.40	0.11	4	0.335				+0.85
L-11					8	0.673	1.46	0.23	0.40	+0.84
L-12					12	1.025				+0.80
S-1	0.8	6.94	3.40	0.11	4	0.218				+1.13
S-2					8	0.494	1.10	0.28	0.33	+1.10
S-3					12	0.776				+1.08
S-4	0.8	5.20	3.40	0.11	4	0.144				+1.67
S-5					8	0.311	0.63	0.32	0.27	+1.60
S-6					12	0.416				+1.60
S-7	0.8	3.47	3.40	0.11	4	0.042				+2.69
S-8					8	0.068	0.19	0.39	0.18	+2.60
S-9					12	0.140				+2.45
M-1	0.8	8.67	2.27	0.11	4	0.210				+1.16
M-2					8	0.481	1.09	0.22	0.43	+1.08
M-3					12	0.747				+1.00
M-4	0.8	8.67	1.70	0.11	4	0.193				+1.35
M-5					8	0.358	0.87	0.24	0.42	+1.35
M-6					12	0.577				+1.24
M-7	0.8	8.67	1.13	0.11	4	0.148				+1.62
M-8					8	0.299	0.67	0.23	0.40	+1.60
M-9					12	0.480				+1.52
M-10	0.8	8.67	0.50	0.11	4	0.112				+1.96
M-11					8	0.225	0.51	0.21	0.47	+1.95
M-12					12	0.348				+1.92
H-1	0.8	8.67	0.00	0.11	4	0.075				0.00
H-2					8	0.180	0.38	0.00	0.59	0.00
H-3					12	0.280			(0.66[f])	0.00

[a] Bulk or benzene solution. [b] 10 ml of aqueous solution. [c] Determined by elemental analysis. [d] Measured in THF at 30 °C. [e] Measured in THF at 25 °C. [f] Measured in benzene at 25 °C. From the intrinsic viscosity, the number average molecular weight of the polymer was calculated as 1.45×10^5 ($Pn = 1.4 \times 10^3$) using the following equation of Krigbaum and Flory (cf.[10]): $[\eta] = 9.52 \times 10^{-5} Mn^{0.744}$.

MAc was continuously studied with a view to obtain more information about the feature of the copolymerization at the oil/water interface.

Interfacial Emulsion Copolymerization of St (M_1) with MAc (M_2). St in organic phase was copolymerized with MAc in aqueous phase, using AIBN, BPO, and KPS as an initiator in the presence of lecithin. St solubilized in organic phase (bulk or benzene solution) and MAc in aqueous phase cannot diffuse into the opposite phase. Both AIBN and BPO are soluble in benzene but insoluble in water. On the contrary, KPS is not soluble in benzene but it is soluble in water. The addition of lecithin to the heterophase system resulted in an emulsification of the system with a reversed micelle, i.e., a water in oil type micelle. The conditions and results of copolymerization are summarized in Table II.

It can be seen from Table II that the copolymers initiated

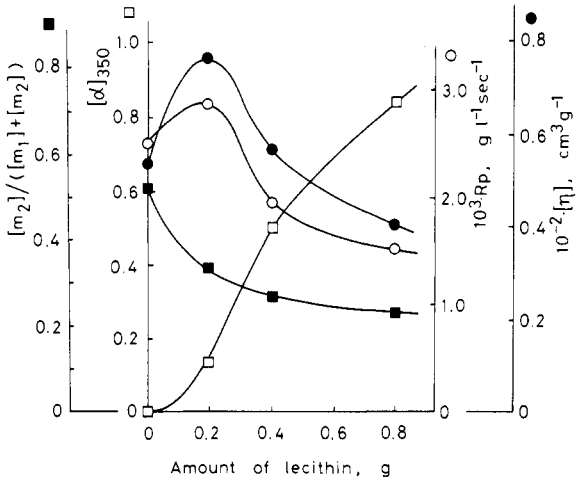


Figure 1. Influence of lecithin on the rate of copolymerization (○), intrinsic viscosity (●), mole fraction of MAc (■), and specific rotation (□) of the copolymer. Organic phase (5 ml): [St] = 8.67 mol L^{-1}. Aqueous phase (10 ml): [MAc] = 3.40 mol L^{-1}, [KPS] = 0.11 mol L^{-1}. Temp: 40 °C. Time: 8 h.

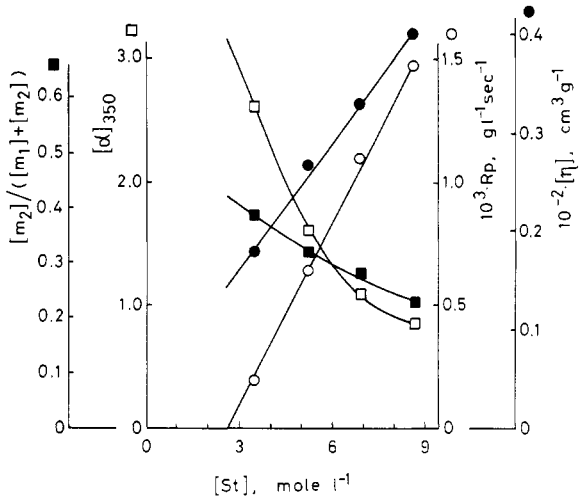


Figure 2. Influence of [St] in organic phase on the rate of copolymerization (○), intrinsic viscosity (●), mole fraction of MAc (■), and specific rotation (□) of the copolymer. Organic phase (5 ml): benzene solution of St. Aqueous phase (10 ml): [MAc] = 3.40 mol L^{-1}, [KPS] = 0.11 mol L^{-1}. Lecithin: 0.8 g (1.02×10^{-3} mol). Temp: 40 °C. Time: 8 h.

by the organic phase soluble initiators (AIBN and BPO) are richer in St mole fraction and lower in specific rotation than that initiated by the aqueous phase soluble initiator (KPS). These copolymers were confirmed not to contain St homopolymer by means of solubility tests. Needless to say, the magnitude of specific rotation of the copolymer can be correlated to the degree of alternation of the monomer units in the copolymer. It is clear from Table II that KPS is more suitable than AIBN and BPO for the interfacial emulsion copolymerization to attain the asymmetric induction.

On the basis of the above data, KPS was used as an initiator for the subsequent emulsion copolymerization.

Influence of the Amount of Lecithin. St was copolymerized with MAc in the above interfacial system, using KPS as an initiator in the presence of various amounts of lecithin. The conditions and results of the copolymerization are shown from runs L-1 to L-12 in Table III and illustrated graphically in Figure 1.

As can be seen from Figure 1, the rate of copolymerization was maximized by controlling the amount of lecithin added to the system. The rate of copolymerization was allowed to decrease by further addition of lecithin. This result indicates that a stable emulsion is formed at a certain concentration of the surfactant. The same behavior was observed for some heterogeneous reactions.[11-14] The intrinsic viscosity of the copolymer was variable with the amount of lecithin in a similar tendency as the rate of copolymerization. The decrease in rate of copolymerization and intrinsic viscosity of the copolymer as a result of the addition of excess lecithin is believed to be due to a difficulty of the monomers to come together at the oil/water interface. The above assumption is supported by the fact that mole fraction of St in the resulting copolymer increased with increasing the amount of lecithin added to the polymerization system. In other words, the apparent monomer reactivity between St and MAc separated in the different phases was depressed by a steric and/or electrostatic hindrance of lecithin at the oil/water interface.

On the other hand, in spite of the considerable deviations of the copolymer composition from 1:1, the specific rotation of the copolymer increased with an increase in the amount of lecithin added to the polymerization system. IR spectra of the copolymers obtained in the presence of lecithin had a similar shape to that obtained in its absence. The specific rotation is believed to be due to an asymmetry induced into the backbone of copolymer chain by lecithin at the micelle–water interface during the propagation step of the interfacial copolymerization.

Influence of St Concentration in Organic Phase. The interfacial copolymerization of St with MAc was carried out under various St concentrations in organic phase. The conditions and the results of the copolymerization are shown from runs L-10 to S-9 in Table III and illustrated graphically in Figure 2.

It can be seen from Figure 2 that the rate of copolymerization and intrinsic viscosity of the resulting copolymer increased linearly with St concentration in organic phase. Under these conditions the copolymerization was found not to proceed at St concentration less than 2.5 mol L^{-1}.

As a matter of course the rate of copolymerization bears a linear relationship with the intrinsic viscosity of the resulting copolymer.

On the other hand, mole fraction of MAc in the copolymer increased in favor of 1:1 copolymer composition with a decrease in St concentration in monomer feed in the organic phase. And the specific rotation of the copolymer increased significantly with an increase in degree of alternation of St and MAc monomer units in the copolymer as a result of decreasing St concentration in the organic phase.

Influence of MAc Concentration in Aqueous Phase. The interfacial copolymerization of St with MAc was carried out under various MAc concentrations in the aqueous phase. The conditions and the results of the copolymerization are shown from runs M-1 to M-12 in Table III and illustrated graphically in Figure 3.

It can be seen from Figure 3 that the rate of copolymerization increased linearly with MAc concentration in aqueous phase. Under these conditions, the polymerization was found to proceed even in the absence of MAC (runs H-1, -2, and -3). That is to say, homopolymerization of St occurred in the emulsion system with a reversed micelle.

Interestingly, the copolymer composition and intrinsic viscosity of the rsulting copolymer were unchanged within the experimental errors, regardless of the changes in MAc concentrations in aqueous phase. In spite of the constant values of copolymer composition and intrinsic viscosity, the specific rotation of the copolymer increased with a decrease in the rate of copolymerization. The effect of lecithin on the asymmetric induction polymerization may be eventually correlated to the

Table IV
Solution Copolymerization of Styrene (M_1) with Maleic Acid (M_2) in THF[a]

Run No.	Lecithin, g	Styrene, mol L^{-1}	Maleic acid, mol L^{-1}	AIBN, mol L^{-1}	Polymn time, h	Yield of polymer, g	$10^3 Rp$, g L^{-1} s^{-1}	$[m_2]/([m_1]+[m_2])^b$	$10^{-2}[\eta]$,[c] cm^3 g^{-1}	$[\alpha]_{350}$[d]
T-1	0.0	1.16	1.16	0.04	8	0.154				0.00
T-2					16	0.316	0.37	0.49	0.17	0.00
T-3					24	0.472				0.00
T-4	0.8 (0.068[e])	1.16	1.16	0.04	8	0.183				+0.50
T-5					16	0.366	0.42	0.51	0.16	+0.54
T-6					24	0.546				+0.52

[a] Total volume: 15 ml. Temp: 40 °C. [b] Determined by elemental analysis. [c] Measured in THF at 30 °C. [d] Measured in THF at 25 °C. [e] In mol L^{-1}.

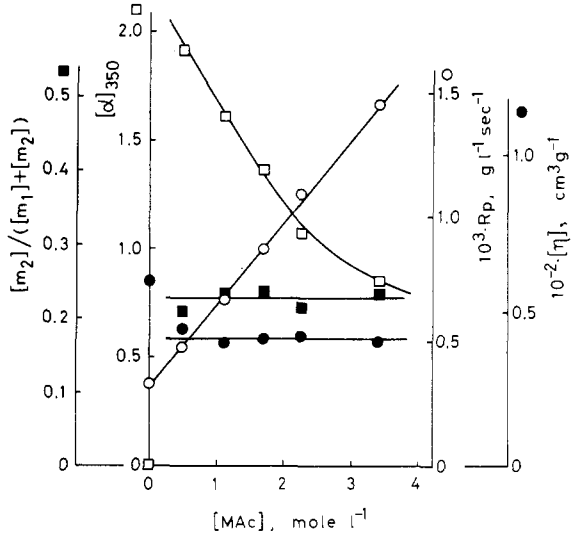


Figure 3. Influence of [MAc] in aqueous phase on the rate of copolymerization (○), intrinsic viscosity (●), mole fraction of MAc (■), and specific rotation (□) of the copolymer. Organic phase (5 ml): [St] = 8.67 mol L^{-1}. Aqueous phase (10 ml): aqueous solution of MAc, [KPS] = 0.11 mol L^{-1}. Lecithin: 0.8 g (1.02×10^{-3} mol). Temp: 40 °C. Time: 8 h.

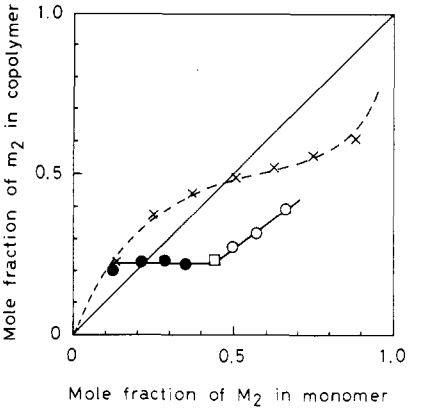


Figure 4. Copolymerization diagrams for the system St (M_1)/MAc (M_2) from the data in Table III: variations of $[M_1]$ in organic phase (○) and $[M_2]$ in aqueous phase (●). (×) Solution copolymerization of M_1 with M_2 in THF at 40 °C in the absence of lecithin.

number of progressing polymer radicals per micelle of lecithin.

Solution Copolymerization of St with MAc. St was copolymerized with MAc using AIBN as an initiator in THF in the presence and the absence of lecithin. The conditions and results of the copolymerization are summarized in Table IV.

In the solution system, one cannot find out any influence of lecithin on the rate of copolymerization, intrinsic viscosity, and copolymer composition except on specific rotation. It was contrary to expectations that lecithin functions as an asymmetric inducing reagent even in the homogeneous system. However, it may be said that the degree of asymmetric induction in the homogeneous system is much lower than that in the emulsion system by considering the amount of lecithin added to the above two distinct systems and the compositions of the resulting copolymers.

The monomer–polymer composition curve for the copolymerization in the solutions system is shown in Figure 4. Monomer reactivity ratios r_1 and r_2 for the system St(M_1)/MAc(M_2) in the solution system were determined approximately as 0.25 and 0.1, respectively.

As described above, the influence of lecithin on the copolymerization of St with MAc was not so significant in the solution system as in the interfacial emulsion system. The above results compared with those for the interfacial emulsion system indicate that lecithin functions effectively as a surface active substance only at the micelle–water interface.[9]

Dependence of the Amount of Lecithin and Monomer Concentration on the Asymmetric Induction. The copolymerization diagram for the above interfacial emulsion system is shown in Figure 4 compared with that for the THF solution system. Evidently the mole fraction of St in the copolymer obtained from the emulsion system was much higher than that obtained from the solution system. Specific rotation of the copolymers is plotted as a function of mole fraction of MAc in the copolymers in Figure 5 from the data in Table III.

Three patterns of relationship can be seen in Figure 5. First, specific rotation of the copolymer increased with a decrease in mole fraction of MAc in the copolymer as a result of increasing the amount of lecithin added to the polymerization system. Second, specific rotation of the copolymer increased with an increase in mole fraction of MAc in the copolymer as a result of decreasing St concentration in monomer feed in the organic phase. Third, specific rotation of the copolymer increased with a constant copolymer composition as a result of decreasing MAc concentration in monomer feed in the aqueous phase.

As described previously, specific rotation of the copolymer can be correlated to the degree of alternation in the copolymer. St is inclined to polymerize with MAc to give an alternating copolymer (see Figure 4). For the solution system, the monomer reactivity ratio, r_2, was calculated as 0.1, which can be regarded as nearly 0, that is, the sequence of MAc–MAc in the copolymer is negligible. For the interfacial emulsion system, as well as for the solution system, r_2 can be nearly 0.

Since mole fraction of MAc in the copolymer cannot exceed

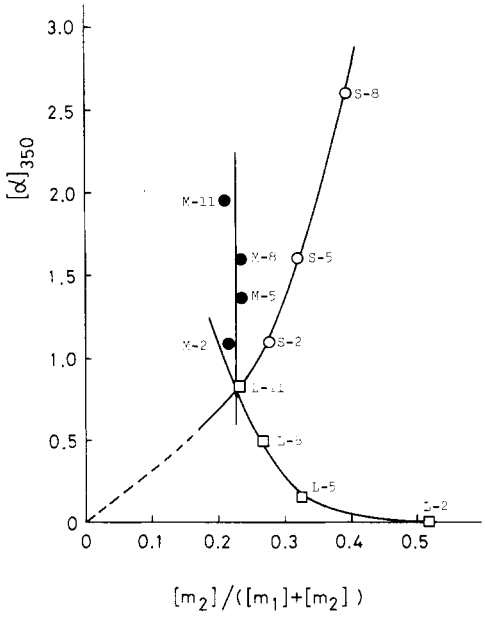


Figure 5. Relation between mole fraction of MAc and specific rotation of the copolymers from the data in Table III: variations of the amount of lecithin (□), $[M_1]$ in organic phase (○), and $[M_2]$ in aqueous phase (●).

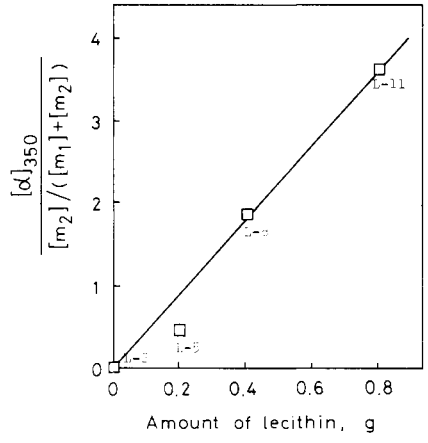


Figure 6. Dependence of the amount of lecithin on the asymmetric induction from the data in Table III.

0.5, the fractional part of St–MAc sequence in the copolymer correponded to the mole fraction of MAc in the copolymer. Asymmetric induction by the copolymerization of St with MAc is caused by an excess of one configuration at the St–MAc sequence in the copolymer. The magnitude of specific rotation may be a measure of asymmetric induction for the copolymer with a constant fractional part of St–MAc sequence. Consequently, the value of specific rotation divided by the mole fraction of MAc in the copolymer, $[\alpha]_{350}/[m_2/(m_1 + m_2)]$, can be correlated to the magnitude of asymmetric induction in St–MAc sequence. Specific rotation per mole fraction of MAc in the copolymer was related to the amount of lecithin and monomer concentration in Figures 6 and 7, respectively, from the data in Table III.

It can be seen from Figure 6 that the magnitude of asymmetric induction varied in proportion to the amount of lecithin added to the polymerization system. On the contrary, Figure 7 shows that the magnitude of asymmetric induction increased as a result of decreasing monomer concentration. In summary, the asymmetric induction was ascertained to be conducted

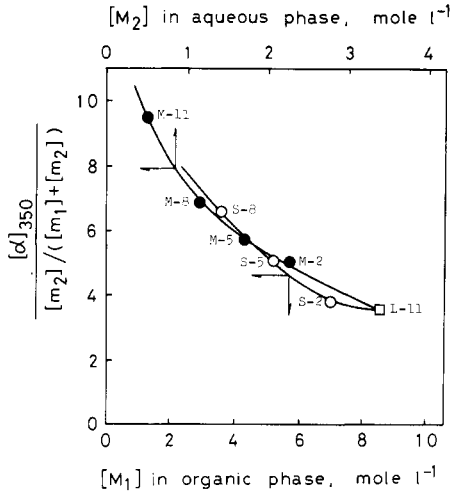


Figure 7. Dependence of monomer concentration on the asymmetric induction from the data in Table III.

conveniently under the conditions in which the rate of copolymerization is relatively low.

Conclusion

In the oil/water interfacial system, St and MAc were set apart in the separate phases which were not miscible with each other. The rate of interfacial copolymerization was enhanced by an adequate amount of lecithin, which emulsified the system. Nevertheless, the application of excess lecithin only made the rate of copolymerization decrease. The "wall" of micelle built up with excess lecithin makes the monomers difficult to come together.

In solution system, the copolymerization of St with MAc resulted in providing an alternating copolymer. Even in the interfacial system without lecithin, the alternating copolymer was obtained. The emulsification of the interfacial system as a result of the presence of lecithin resulted in variation in the composition of resulting copolymer. That is, mole fraction of St in the copolymer could be increased by the addition of lecithin to the polymerization system. This behavior indicates that apparent monomer reactivity ratios are allowed to change by the "wall" of lecithin micelle.

Furthermore, the interfacial copolymerization of St with MAc in the presence of lecithin provided an optically active copolymer. This optical activity of the St–MAc copolymer is due to the asymmetry induced by the chirality of lecithin, though the configuration in the backbone of the polymer chain is indistinct for the present.

References and Notes

(1) P. Walden, *Z. Phys. Chem.*, **20**, 383 (1896).
(2) C. S. Marvel, R. L. Frank, and E. Prill, *J. Am. Chem. Soc.*, **65**, 1647 (1943).
(3) C. S. Marvel and C. G. Overberger, *J. Am. Chem. Soc.*, **68**, 2106 (1946).
(4) C. G. Overberger and L. C. Palmer, *J. Am. Chem. Soc.*, **78**, 666 (1956).
(5) N. Beredjick and C. Schuerch, *J. Am. Chem. Soc.*, **78**, 2646 (1956); **80**, 1933 (1958).
(6) G. J. Schmitt and C. Schuerch, *J. Polym. Sci.*, **45**, 313 (1960).
(7) H. Yamaguchi and Y. Minoura, *J. Polym. Sci., Part A-1*, **8**, 1467 (1970).
(8) N. Sakota, K. Kishiue, S. Shimada, and Y. Minoura, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1787 (1974).
(9) T. Doiuchi and Y. Minoura, unpublished paper.
(10) W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **11**, 37 (1953).
(11) E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, **8**, 271 (1970).
(12) E. H. Cordes and C. Giltler, *Progr. Bioorg. Chem.*, **2**, 1 (1973).
(13) I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, *Russ. Chem. Rev. (Engl. Transl.)*, **42**, 787 (1973).
(14) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Chemistry", Academic Press, New York, N.Y., 1975.