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

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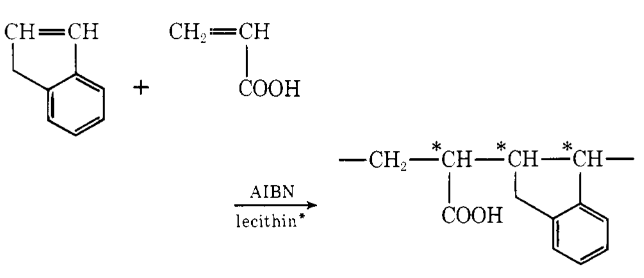
ABSTRACT: The copolymerization of indene with acrylic acid was studied in the presence and absence of lecithin, using 2,2′-azobis(isobutylo)nitrile (AIBN) in benzene. The rate of copolymerization was found to be enhanced by addition of lecithin. Further, a slightly optically active copolymer was obtained 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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Table I
Copolymerization of Indene (M_1) with Acrylic Acid (M_2)[a]

In the absence of lecithin					In the presence of lecithin[b]				
$[m_1]$, mol L^{-1}	$[m_2]$, mol L^{-1}	$10^5 Rp$, g L^{-1} s^{-1}	$[m_1]/([m_1] + [m_2])$[c]	$10^{-2}[\eta]$,[d] cm^3 g^{-1}	$10^5 Rp$, g L^{-1} s^{-1}	Yield of polymer, g (h)	$[m_1]/([m_1] + [m_2])$[c]	$10^{-2}[\eta]$,[d] cm^3 g^{-1}	$[\alpha]_{400}$[e]
0	3.44	62.2	0.00		24.1	0.758 (90)	0.00		0.00
						1.033 (114)			0.00
0.42	3.02	12.2	0.11		26.9	0.898 (90)	0.11		−0.22
						0.102 (114)			−0.19
0.86	2.58	8.4	0.23	0.45	27.7	0.901 (90)	0.21	0.22	−0.27
						1.133 (114)			−0.28
1.29	2.15	6.7	0.29		29.1	0.758 (90)	0.27		−0.30
						1.186 (114)			−0.34
1.72	1.72	6.0	0.32	0.25	26.1	0.825 (90)	0.31	0.17	−0.38
						1.063 (114)			−0.43
2.15	1.29	5.1	0.38		22.8	0.942 (114)	0.35		−0.50
						1.220 (162)			−0.46
2.58	0.86	4.2	0.41	0.16	19.1	0.820 (114)	0.37	0.12	−0.58
						1.025 (162)			−0.61
3.02	0.42	2.9	0.47		10.5	0.616 (162)	0.43		−0.75
						0.744 (210)			−0.84

[a] $[m_1] + [m_2] = 3.44$ mol L^{-1} and [AIBN] $= 1.0 \times 10^{-2}$ mol L^{-1}. Total volume: 10 mL. Polymerization temp, 40 °C. [b] [Lecithin] $= 6.41 \times 10^{-2}$ mol L^{-1}. [c] Determined by elemental analysis. [d] Measured in methanol at 35 °C. [e] Measured in methanol at 25 °C. $c = 5.5$ g dL^{-1}, $l = 0.1$ dm.

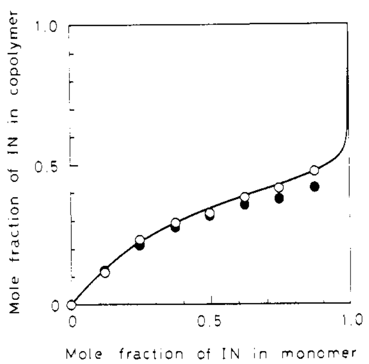

Figure 1. Monomer–copolymer composition curve for the copolymerization of indene (IN, m_1) with acrylic acid (AAc, m_2). [IN] + [AAc] = 3.44 mol L^{-1} and [AIBN] = 1.0×10^{-2} mol L^{-1} in benzene; temperature 40 °C; (○) [lecithin] = 0; (●) [lecithin] = 6.41×10^{-2} mol L^{-1}.

Physical Measurements. 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

The copolymerization of IN with AAc was carried out in benzene in the presence of a constant amount of lecithin and in its absence. The total monomer concentration was kept constant. The detailed description of the conditions and the results of the copolymerization are summarized in Table I.

The IR spectra of the optically active copolymer had peaks at 1720 (COOH), 1480 (indene), and 760 cm^{-1} (indene) and were the same as the optically inactive copolymer obtained in the absence of lecithin.

Figure 1 shows the monomer–copolymer composition curve for the copolymerization of IN (M_1) with AAc (M_2) in the presence and absence of lecithin. From the composition curve for the copolymerization in the absence of lecithin, the monomer reactivity ratios, r_1 and r_2, were calculated as 0.005 and 0.90, respectively, by using the method of Mayo and Lewis.[5]

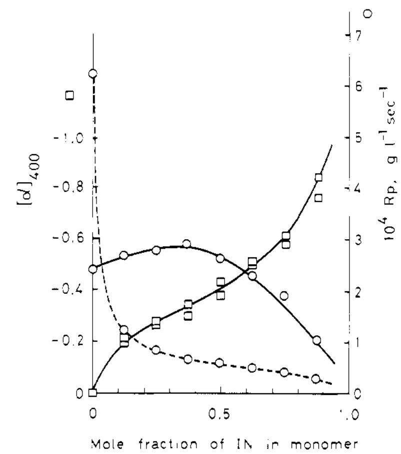

Figure 2. Influence of monomer composition on the rate of copolymerization (○) and specific rotation of the copolymer (□). [IN] + [AAc] = 3.44 mol L^{-1}, [AIBN] = 1.0×10^{-2} mol L^{-1}, and [lecithin] = 6.41×10^{-2} mol L^{-1} in benzene; temperature 40 °C, (--○--) in the absence of lecithin.

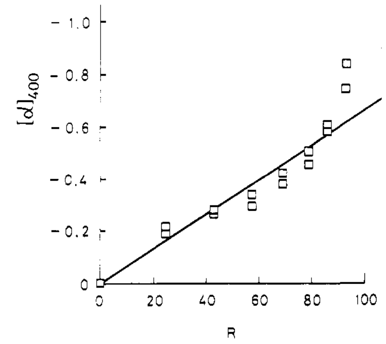

Figure 3. Relationship between the run number of dyad sequences of -IN·AAc- and -AAc·IN- per 100 monomer units, R, and specific rotation of the copolymer, $[\alpha]_{400}$.

The composition of monomer concentration at the site of copolymerization in the presence of lecithin may differ from that in its absence. The monomer–copolymer composition data in Figure 1 may be meaningless in the strict sense of the term. Nevertheless, Figure 1 shows that the presence of lecithin in the system brings about little influence on the monomer reactivity ratios in appearance throughout the copolymerization. Therefore the reactivity ratios in the presence of lecithin are thought to bear a close resemblance to those in the absence of it.

As shown in Figure 2, the rate of copolymerization decreased with an increase in mole fraction of IN in monomer feed in the absence of lecithin. This result can be accounted for by the difference in reactivities of the two monomers, that is, AAc is more susceptible to homopolymerization than IN. Interestingly, the rate of copolymerization was increased by the addition of lecithin, except in the case of homopolymerization of AAc. The rate enhancement by lecithin may be due to a preferable orientation of IN and AAc for the copolymerization.

In addition to the rate enhancement, the copolymer obtained in the presence of lecithin had an optical activity, the sign of which was opposite to that of lecithin. The optical rotatory dispersion (ORD) measurements for the copolymers gave negative plain curves, from which λ_0 values were calculated as about 220 nm, using the simple Drude equation.[6]

Figure 2 also shows specific rotation of the copolymer as a function of the mole fraction of IN in the monomer feed. The absolute value of the specific rotation was increased with an increase in IN monomer units of the copolymer as a result of increasing mole fraction of IN in monomer feed. Needless to say, the asymmetric carbon atoms occur in the copolymers only where IN–AAc or AAc–IN bonds are present. Consequently, the specific rotation of the copolymer must have an interrelation with the run number.[7] The run number of dyad sequences of -IN·AAc- and -AAc·IN- per 100 monomer units, *R*, is defined as the following equation:

$$R = \frac{200}{2 + r_1x + r_2/x}$$

where x is molar ratio of feed monomers and r_1 and r_2 are monomer reactivity ratios. Figure 3 shows the relationship between the specific rotation of the IN/AAc copolymer and its run number, using r_1 and r_2 values calculated for the copolymerization in the absence of lecithin for the reason described already. In accordance with the relationship, the plot is found to be approximately linear.

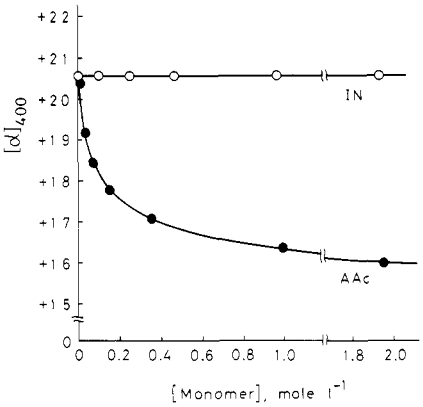

Figure 4. Variation in specific rotation of lecithin: [lecithin] = 3.1 × 10^{-2} mol L^{-1} (*c* 2.43, benzene); temperature 25 °C.

The asymmetric induction is undoubtly caused by the electrostatic interaction between the polar monomer, AAc, and the polar head group of lecithin. Figure 4 shows the variation in specific rotation of lecithin by addition of AAc. As can be seen from Figure 4, the nonpolar monomer, IN, does not affect the specific rotation of lecithin, whereas the polar monomer, AAc, decreases significantly the specific rotation. This result indicates that there is a fair electrostatic interaction between AAc and lecithin. In conclusion, the asymmetric induction can be considered to be conducted by a stereospecific copolymerization of IN with AAc affected by the chiral surface active substance, lecithin.

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The Carbon-13 Nuclear Magnetic Resonance Methyl Shift in Models of Regioirregular Polypropylene[1]

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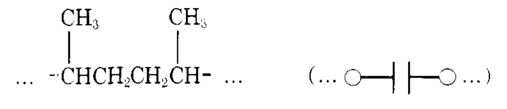
ABSTRACT: Model compounds for irregular arrangements of monomer units in polypropylene have been synthetized. The ^{13}C-NMR spectra have been assigned, considering also the steric structure of the hydrocarbons. An empirical relationship for predicting the ^{13}C methyl shift is proposed, based on constitution and configuration.

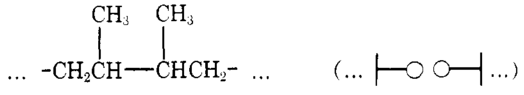
I. Introduction

The highly isotactic polymers of propylene, such as those obtained in the presence of catalytic systems consisting of violet titanium trichloride and organometallic compounds of aluminium, show a very regular chemical arrangement of the monomer units, i.e., head-to-tail.

On the contrary a small amount of head-to-head and tail-



$$\ldots\ \text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}CH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}\ \ldots$$



$$\ldots\ \text{-}CH_2\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}H}CH_2\text{-}\ \ldots$$

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