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Properties

Radical Copolymerization of Optically Active Acryloyl-D-Phenylglycine Methyl Ester with Methyl Methacrylate or with Methyl Acrylate in Optically Active Solvent

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Summary

The rate of radical copolymerization of optically active acryloyl-D-phenylglycine methyl ester(APM) with methyl methacrylate(MMA) or with methyl acrylate(MA) was dilatometrically measured in optically active solvents, D- or L-ethyl mandelate. The copolymerization rate of D-monomer in D-solvent was higher than that in L-solvent. The origin of the difference in the copolymerization rate was discussed using data of UV and ^{13}C-NMR chemical shift and spin lattice relaxation time, T_1, and the asymmetric solvent effect was concluded to be due to the difference in the interaction between propagating radical and solvent.

Introduction

We have investigated the solvent effect on the rate of free radical polymerization of vinyl compounds, and explained the solvent effect in terms of the interaction between the propagating radical and aromatic solvents(1, 2). If such an interaction is an important factor for the reaction control in the radical polymerization, the effect of asymmetric solvent on the polymerization rate of optically active monomer and the tacticity of the polymer might be expected. In recent years, some studies on the asymmetric solvent effect on the tacticity have been reported(3-12), but the studies of asymmetric solvent effect on the radical polymerization rate are extremely limited(13). In this paper, the copolymerization rates of optically active monomer with MMA or with MA in D- and L-ethyl mandelate have been studied.

Results and Discussion

Owing to the poor solubility of optically active monomer in ethyl mandelate, the homopolymerization rate could not be measured by dilatometry in the optically active solvents. Therefore, the copolymerization systems were chosen and in each systems the rate in D-solvent was compared with that in L-solvent. The measurements of the rates(R_p) were performed

Table 1. Rate of copolymerization in optically active solvents[a]

M_1	M_2	$R_p \times 10^5$/Ms^{-1} in D-solvent	$R_p \times 10^5$/Ms^{-1} in L-solvent	$\frac{R_p(D)}{R_p(L)}$
D-APM	MMA	6.42±0.24	3.76±0.24	1.7
D-APM	MA	2.34±0.07	1.85±0.10	1.3

a: $[AIBN]=3\times10^{-3}M$, $[M_1]=0.5M$, $[M_2]=1.0M$. 40°C.

twice in each copolymerization. The reproducibility of the data obtained was good enough for the discussion on the influence of the asymmetric solvent on R_p. The results are shown in Table 1. In the system, D-APM-MMA, the copolymerization rate in D-solvent was 1.7 times as large as that in L-solvent and in the system, D-APM-MA, the rate in D-solvent was 1.3 times as large as that in L-solvent. These results clearly indicate that the copolymerization rate was influenced by the asymmetric solvent.

The following factors are considered as the origin for such an asymmetric solvent effect: the interaction between polymer and solvent, between monomer and solvent, and between the propagating radical and solvent. If the effect was due to the asymmetric interaction between polymer and solvent, the difference in the viscosity of the polymer in D- and L-solvents may be expected. But the intrinsic viscosity of the polymers has the same value in both D- and L-solvents within the experimental error.

Table 2. T_1(sec.) of D-APM[1]

solvent	a	b	c	d	e
D	2.4	4.0	3.2	0.12	0.58
L	2.5	3.2	2.7	0.13	0.68

[1] Monomer 5%, C_6D_6 10%.

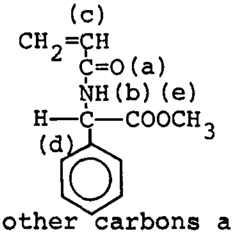

Table 3. The influence of asymmetric solvents on the copolymer compositions.

D-solvent			L-solvent		
APM	:	MMA	APM	:	MMA
22±3	:	78±3	19±5	:	81±5

Next the interaction between monomer and solvent was examined by UV and NMR spectroscopies(chemical shift and T_1) of the monomers in D- and L-solvents. No asymmetric solvent effect was detected in the UV spectra and the chemical shift in the ^1H and ^{13}C NMR spectra, but the difference in T_1 of monomers between in D- and L-solvents was detected as shown in Table 2. T_1 of the carbonyl carbon (b) of D-APM in D-solvent is about 1 sec. longer than that in the L-solvent, although the T_1's for other carbons are almost similar in D- and L-solvents. The results seem to show that the interaction between monomer and solvent is one of factors of the asymmetric solvent effect. However, considering from the fact that no solvent effect was detected in UV and NMR chemical shift, the interaction between monomer and solvent may not be a predominant factor for the solvent effect. Copolymerizations of D-APM(M_1) with MMA (M_2) were performed in both solvents at 60°C. The copolymer composition shown in Table 3 are the average values of three runs with 29-33% conversion, respectively. The composition of the copolymer obtained in D-solvent was the same within the experimental error as that in L-solvent. The result shows that the monomer reactivity ratios(k_{11}/k_{12} and k_{22}/k_{21}) are the same in both solvents. Since the value of $k_p(k_{22})$ for MMA is not influenced by the asymmetric property of the solvent, the reactivity of D-APM with a MMA radical end(k_{21}) should be the same in both solvents. On the other hand, k_{11} for D-APM in D-solvent is considered to be larger than that in L-solvent, because the difference in R_p observed between both solvents is probably ascribed to that in $k_p(k_{11})$. This indicates that k_{12} in D-solvent must be larger than that in L-solvent. Accordingly, the reactivity of D-APM radical is concluded to be influenced by the asymmetric property of solvents.

Experimental

D-APM($[\alpha]_D^{25}$=-194.8°, c 1, methanol) was prepared from acryloyl chloride and the corresponding α-amino acid methyl ester hydrochloride(14). Ethyl mandelates(L:$[\alpha]_D^{25}$=-135°, D: $[\alpha]_D^{25}$=137°, c 1, chloroform) were prepared by the esterification of the corresponding mandelic acid and purified by distillation(15,16). Photopolymerization rates were measured by dilatometer in vacuo with AIBN initiator at 40°C under irradiation, using an Ushio 250W high pressure mercury lamp with filters(Toshiba UV-31, and UV-DIC) for 365nm. Copolymer compositions were estimated from the nitrogen content in elementary analysis of the copolymers. NMR spectra were recorded on a Model JEOL JNM-FX100 Fourier transform NMR spectrometer, and ^{13}C-T_1 was measured in benzene-d_6 at 60°C by inversion-recovery method. Samples for T_1 measurement were contained in 10mm tubes, and degassed by repeated melting and freezing under vacuum, filled with dry nitrogen, and sealed.

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