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Radical Polymerization Behavior of *N*-Acryloyl-2,2-dimethyl-5(*R*)-phenyl-1,3-oxazolidine

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ABSTRACT: The radical polymerization of *N*-acryloyl-2,2-dimethyl-5(*R*)-phenyl-1,3-oxazolidine (ADPO) was investigated kinetically and by means of ESR spectroscopy. The polymerization of ADPO was carried out in benzene with dimethyl 2,2′-azobis(isobutyrate) (MAIB) as an initiator in the temperature range of 50−70 °C. From the Arrhenius plot of the initial polymerization rate (R_P), the overall activation energy of the polymerization was calculated to be 82 kJ mol^{-1}. R_p at 60 °C was expressed by $R_p = k[\text{MAIB}]^{0.5}[\text{ADPO}]^{1.0}$. Thus the polymerization of ADPO was found to show the usual kinetic behavior. An ESR spectrum was observed in the actual polymerization, which was ascribed to the propagating poly(ADPO) radical. Using the spectrum, the concentration of the propagating polymer radical was determined and the rate constants of propagation (k_p) and termination (k_t) of ADPO were estimated at 50, 60, and 70 °C. From the Arrhenius plots of k_p and k_t, the activation energies of propagation and termination were estimated. Furthermore the copolymerization of ADPO (M_1) with styrene (M_2) was also examined at 60 °C, and the following copolymerization parameters were obtained using a curve-fitting method; $r_1 = 0.22$, $r_2 = 0.76$ (SD = 0.01), $Q_1 = 0.45$, $e_1 = +0.53$. The rate constants of cross-propagations of copolymerization were also estimated.

Introduction

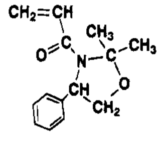
The control of stereochemistry in free-radical polymerization is very difficult due to the electrically neutral nature of the intermediate being free from interacting species such as a counterion. The radical polymerization of methacrylate monomers is well-known to yield syndio-rich polymers because of steric repulsion between the substituents of monomers and propagation polymer radicals in the propagating step.[1] Some methacrylates of much bulkier alcohols such as trityl[2], diphenyl-2-pyridylmethyl,[3] and 1-phenyldibenzosuberyl[4] alcohols were, however, reported to be radically polymerized to yield highly isotactic polymers. Among them the radically formed poly(1-phenyldibenzosuberyl methacrylate) is quantitatively isotactic.

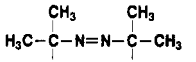
Recently, *N*-acryloyl-2,2-dimethyl-5(*R*)-phenyl-1,3-oxazolidine (ADPO), being an acrylamide derivative, was also observed to undergo stereocontrolled free-radical polymerization to give a highly isotactic (92%, diad) polymer by Porter et al.[5] This was explained as the result of facial selectivity caused by the chiral auxiliary in the addition of the monomer to the growing polymer radical.

It is of great interest to elucidate kinetic behaviors of the isotactic-specific radical polymerization of these monomers because their propagating polymer radicals are possible to take a helical conformation in the polymerization systems.[1−5]

More recently we have found that the radical polymerization of ADPO involves ESR-observable propagating polymer radicals under the actual polymerization conditions. In the present paper we have studied kinetically and ESR spectroscopically the polymerization of ADPO with dimethyl 2,2′-azobis(isobutyrate) (MAIB) in benzene and also examined the properties of obtained poly(ADPO).

Experimental Section


ADPO


$$H_3C-\underset{COOCH_3}{\overset{CH_3}{C}}-N=N-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_3$$
MAIB

ADPO was prepared in the following manner described by Porter et al.[5] D-(−)-α-Phenylglycine was reduced with lithium aluminum hydride in tetrahydrofuran (THF) to yield D-(−)-α-phenylglycinol (PGN). PGN was purified by recrystallization from an ethyl acetate−*n*-hexane mixture (mp 74−76 °C). PGN was allowed to react with acetone in the presence of $MgSO_4$ and then further with acryloyl chloride in methylene chloride in the presence of *N*-methylmorpholine to yield ADPO. A solution of crude ADPO in an ethyl acetate−hexane mixture was passed through a silica gel column. Pure ADPO monomer was obtained by recrystallization from ethyl acetate (mp 81−82 °C).

Dimethyl 2,2′-azobis(isobutyrate) (MAIB) was recrystallized from methanol. Solvents were purified by the usual methods.

Polymerization and copolymerization of ADPO were carried out in a degassed and sealed glass tube with shaking. The resulting polymers were isolated by pouring the polymerization mixture into a large excess of methanol.

The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the polymer and copolymer were determined by size-exclusion chromatography (SEC) with a calibration by polystyrene (poly(St)) standards. So, the $\bar{M}_n$ and $\bar{M}_w$ values obtained are the poly(St) reduced ones. SEC was recorded by a Tosoh HLC-802A at 38 °C with THF as the carrier.

An ESR spectrum of the polymerization mixture in a degassed and sealed ESR tube was recorded with JEOL-JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity.

Dynamic thermogravimetry (TG) was carried out in a N_2 stream (flow rate, 20 mL/min) with a Shimadzu TG-50 thermogravimeter at a heating rate of 10 °C/min. A differential scanning calorimeter (DSC) (Shimadzu DSC-50) was used for examination of the thermal behavior of poly(ADPO) (heating rate, 10 °C/min).

The specific rotations ($[\alpha]_D$) of ADPO and of its polymer were measured by using a Jasco-DIP 360 digital polarimeter at room temperature.

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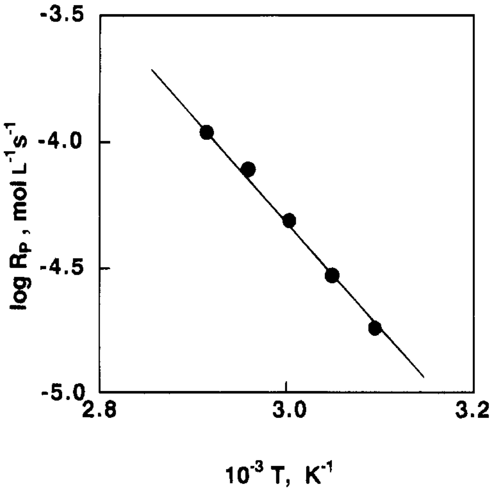


Figure 1. Dependence of the polymerization rate (R_p) on the polymerization temperature.

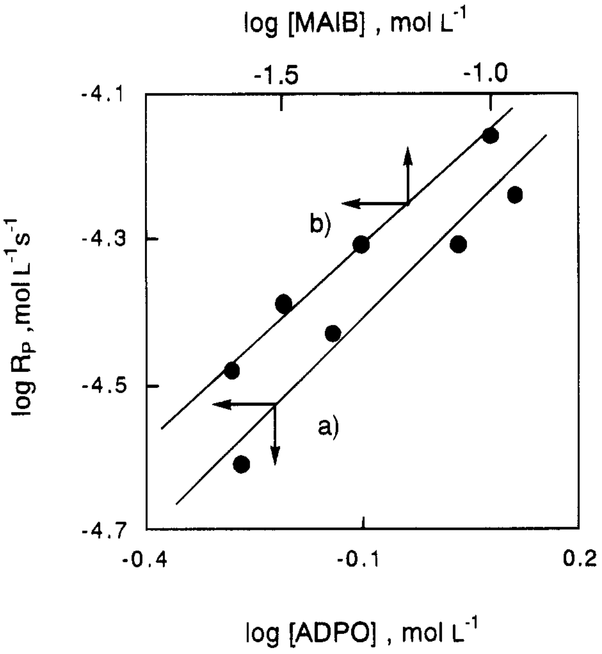


Figure 2. Dependence of the polymerization rate (R_p) on the (a) ADPO and (b) MAIB concentrations at 50 °C.

Results and Discussion

Kinetic Study. The radical polymerization of ADPO with MAIB in benzene was carried out in the temperature range of 50–70 °C. The polymerization proceeded in a homogeneous condition. The polymer yield (up to 16%) in the initial stage of the polymerization increased almost proportionately with time without any induction period. Figure 1 shows the Arrhenius plot of the initial polymerization rate (R_p) estimated from the time–conversion plot at each temperature. From the slope of the straight line in Figure 1, the overall activation energy (E_a) of the polymerization was estimated to be 82 kJ mol^{-1}. The value is similar to those (84 kJ mol^{-1}) for the polymerizations of methyl methacrylate (MMA) and styrene (St) with azobis(isobutyronitrile) (AIBN).[6] MAIB and AIBN have similar activation energies of decomposition.[7]

Figure 2 shows the effects of the monomer (a) and initiator (b) concentrations on R_p. From the relationship between R_p and the ADPO concentration, the dependence of R_p on the ADPO concentration was determined to be first order. Furthermore, R_p was found to be proportional to the square root of the MAIB concentration. From the above results, R_p is expressed by eq 1.

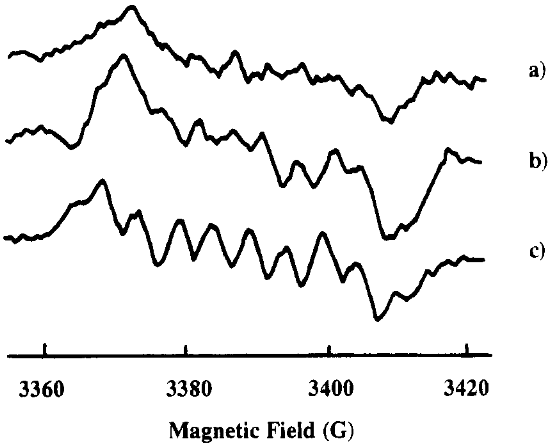


Figure 3. ESR spectra observed in the polymerization of ADPO with MAIB in benzene at (a) 50 °C, (b) 60 °C, and (c) 70 °C; [ADPO] = 1.08 mol L^{-1}, [MAIB] = 5.00×10^{-2} mol L^{-1}.

Table 1. Propagating Polymer Radical Concentration ([P•]), Rate Constants of Initiation (k_df), Propagation (k_p), and Termination (k_t), and Initiator Efficiency (f) in the Polymerization of ADPO with MAIB in Benzene[a]

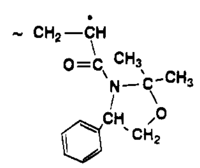
temp (°C)	10^7[P•] (mol L^{-1})	10^5k_df (s^{-1})	f[b]	k_p (L mol^{-1} s^{-1})	$10^{-5}k_t$ (L mol^{-1} s^{-1})
50	8.8	0.137	0.60	19.4	1.7
60	16.2	0.52	0.63	28.2	2.0
70	27.2	2.03	0.69	37.1	2.7

[a] [ADPO] = 1.08 mol L^{-1}. [b] Calculated using k_d (s^{-1}) = $5.69 \times 10^{12} \exp(-120.1 \text{ kJ}/RT)$.[7]

$$R_p = k[\text{MAIB}]^{0.5}[\text{ADPO}]^{1.0} \quad (\text{at } 60\ °\text{C}) \qquad (1)$$

The equation indicates that the polymerization of ADPO proceeds according to the ideal kinetics involving bimolecular termination.

ESR Study. Figure 3 shows ESR spectra observed in the polymerization of ADPO with MAIB in benzene at 50, 60, and 70 °C. The spectra (g = 2.003) observed are ascribable to the propagating poly(ADPO) radical (**I**). Since the spectrum was almost unchanged in shape and intensity during ESR measurement, the propagating polymer radical was confirmed to reach a stationary state. So, we have attempted to determine the absolute rate constants for elementary reactions. The stationary concentration of the propagating polymer radical ([P•]) was determined by computer double integration of the ESR spectra, where 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), a stable radical,[8] was used as a standard in the same medium. Table 1 lists the results obtained. Using R_p and [P•] determined, the values of k_p were estimated according to eq 2 for the stationary state polymerization and are also shown in Table 1.



(I)

$$R_p = k_p[\text{P}^\bullet][\text{ADPO}] \qquad (2)$$

In order to estimate the rate constant of termination (k_t), the initiation rate is required to be determined. The k_df value was estimated in the following manner de-

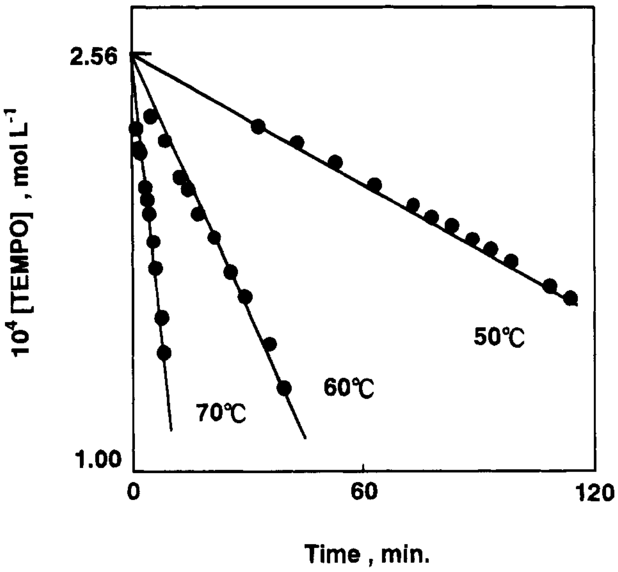
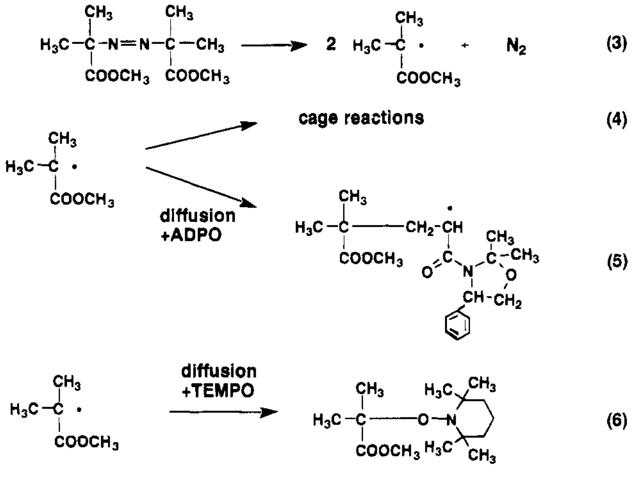


Figure 4. Relationship between reaction time and [TEMPO] during the polymerization of ADPO with MAIB in benzene; [ADPO] = 1.08 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}, [TEMPO] = 2.56 × 10^{-4} mol L^{-1}.

scribed previously,[9] where k_d = rate constant of MAIB decomposition and f = initiator efficiency.

MAIB decomposes into 1-(methoxycarbonyl)-1-methylethyl radicals and nitrogen (eq 3). Some of the primary



radicals are deactivated through cage reactions (eq 4). The others diffuse through solvent cage to initiate the polymerization (eq 5). When TEMPO is present in the polymerization system, the solvent-cage escaping primary radicals are trapped by TEMPO to yield a coupling product (eq 6) before they initiate the polymerization.

Even if the primary radicals add to the monomer before they react with TEMPO, the resulting radicals (eq 5) can also be trapped by TEMPO quantitatively. So, determination of the disappearance rate of TEMPO leads to an estimation of the k_df values.

The disappearance of TEMPO was followed by ESR. Figure 4 shows plots of the TEMPO concentration vs reaction time during decomposition of MAIB in the polymerization system. From the slope of the plot, the disappearance rate (R_t) of TEMPO was estimated. Using R_t and k_d calculated from eq 7 reported for MAIB,[7] the k_df and then the f values were determined according to $R_t = 2k_df$[MAIB] and are presented in Table 1.

$$k_d\,(\mathrm{s}^{-1}) = 5.69 \times 10^{12} \exp(-120.1\ \mathrm{kJ}/RT) \qquad (7)$$

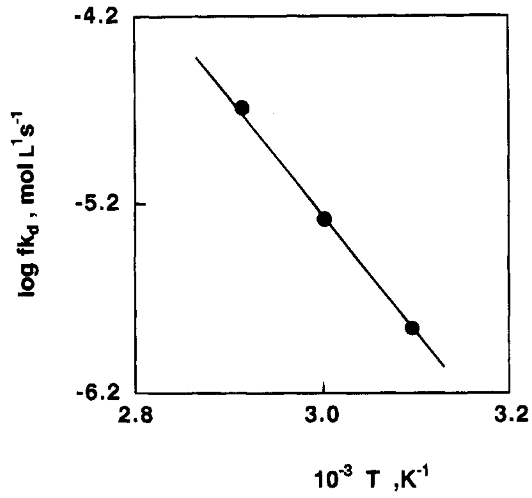


Figure 5. Dependence of the initiation rate constant (fk_d) on the polymerization temperature.

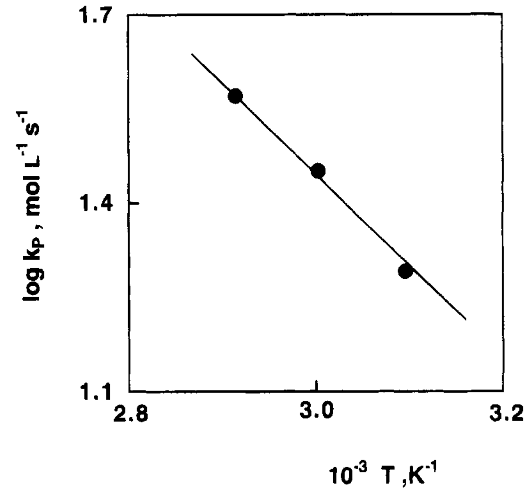


Figure 6. Dependence of the propagation rate constant (k_p) on the polymerization temperature.

As mentioned above, the present polymerization involves the usual bimolecular termination. So the k_t values were also calculated according to eq 8 using [P$^\bullet$] and k_df values and are listed in Table 1.

$$2k_df[\mathrm{MAIB}] = k_t[\mathrm{P}^\bullet]^2 \qquad (8)$$

Thus, the values of f, k_p, and k_t were determined at different temperatures. Figures 5–7 illustrate the Arrhenius plots of k_df, k_p, and k_t. From the slopes of the plots, the activation energies of initiation (E_i), propagation (E_p), and termination (E_t) were calculated to be 124, 29, and 21 kJ mol^{-1}, respectively. The E_i value (124 kJ mol^{-1}) is close to the activation energy (120 kJ mol^{-1}) reported for the MAIB decomposition in benzene.[7] Using these values of the activation energies, the overall activation energy of the polymerization could be estimated to be 80.5 kJ mol^{-1} according to eq 9 which holds for the present polymerization as an ideal radical polymerization.

$$E_a = E_p + (E_i - E_t)/2 \qquad (9)$$

Thus, the calculated value is closely similar to the observed one (82 kJ mol^{-1}) described above.

Table 2 compares the rate constants, activation energies, and frequency factors for the elemental reactions of ADPO with those of some vinyl monomers. The k_p value of ADPO is much smaller than those of MMA and

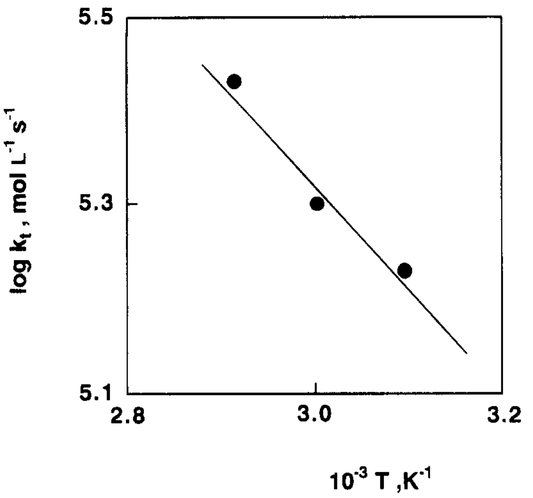


Figure 7. Dependence of the termination rate constant (k_t) on the polymerization temperature.

Table 2. Activation Energy (E), Frequency Factor (A), and Rate Constants for the Elemental Reactions of ADPO and Some Vinyl Monomers

	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k_p, k_t (L mol^{-1} s^{-1})	ref
initiation	124			this work
for k_p				
ADPO	28.3	7.32×10^5	19.4 (50 °C)	this work
MMA	18.1	4.92×10^5	582 (50 °C)	10
St	30.8	1.99×10^7	209 (50 °C)	10
AAm	18.8	7.50×10^7	43000 (30 °C)	12
DMAAm			27200 (30 °C)	13
for k_t				
ADPO	21.4	4.90×10^8	1.70×10^5 (50 °C)	this work
MMA	11.9	1.36×10^9	1.22×10^7 (30 °C)	11
St	6.3	7.10×10^8	5.02×10^7 (30 °C)	11
AAm	10.9	2.61×10^{10}	3.50×10^8 (30 °C)	12
DMAAm			3.54×10^9 (30 °C)	13

Table 3. Molecular Weights of Poly(ADPO) and Polydispersities

temp (°C)	[ADPO] (mol L^{-1})	10^2[MAIB] (mol L^{-1})	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
50	1.08	5.0	2.4	1.8
55	1.08	5.0	2.2	1.7
60	1.08	5.0	1.8	1.7
65	1.08	5.0	1.3	1.6
70	1.08	5.0	1.2	1.6
60	0.54	5.0	1.0	1.5
60	0.72	5.0	1.3	1.6
60	1.08	5.0	1.8	1.7
60	1.30	5.0	2.0	1.7
60	1.08	2.5	2.2	1.7
60	1.08	3.3	2.0	1.7
60	1.08	5.0	1.8	1.7
60	1.08	10.0	1.4	1.6

St[10,11] and 3 orders smaller than those of acrylamide (AAm)[12] and *N,N*-dimethylacrylamide (DMAAm).[13]

As mentioned above, the homogeneous polymerization system of ADPO with MAIB was found to involve ESR-observable propagating polymer radicals, indicating a slow bimolecular termination. As was expected, the k_t value of ADPO is 2 orders smaller than those of MMA and St,[10,11] and it is 3 or 4 orders smaller than those of AAm[12] and DMAAm.[13] The low k_t of ADPO seems to stem from both a high E_t and a low-frequency factor.

The low k_p and k_t values of ADPO come probably from the rigidity of the propagating poly(ADPO) radical chain which may be caused by the bulky side group or by the helical structure of isotactic poly(ADPO).

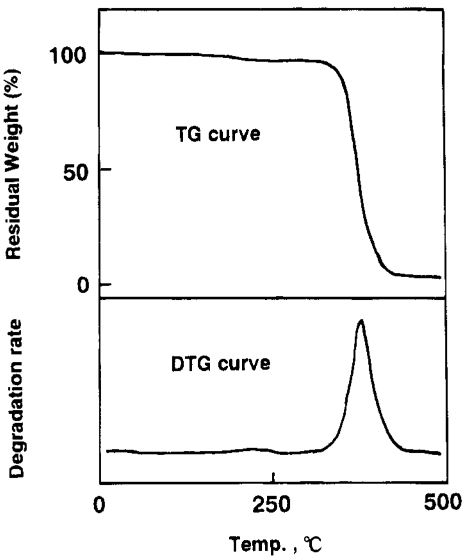


Figure 8. TG and DTG curves of poly(ADPO).

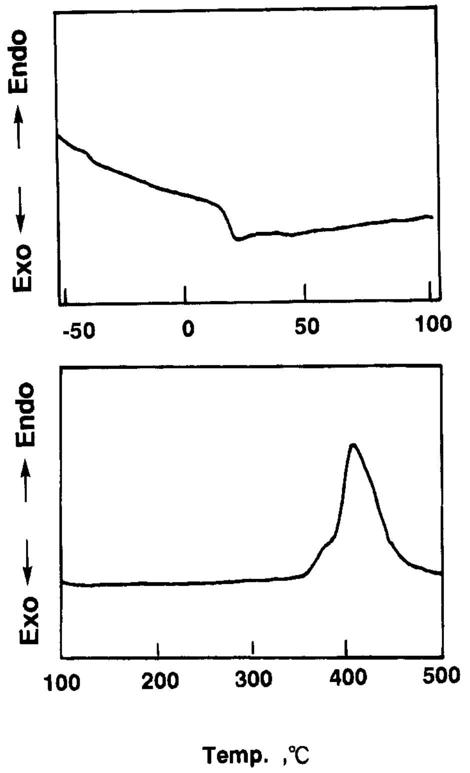


Figure 9. DSC curve of poly(ADPO).

Polymer Characterization. Table 3 summarizes the molecular weights and molecular weight distributions of the polymers formed under different polymerization conditions. $\bar{M}_n$ increased with increasing monomer concentration and with decreasing initiator concentration in a manner similar to that in the usual radical polymerization. The $\bar{M}_w/\bar{M}_n$ (1.5−1.7) is similar to those of the usual radical polymerization.

Figure 8 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of poly(ADPO) obtained in benzene. The polymer is not thermally so stable. Rapid decomposition began near 300 °C. The maximum on the DTG curve was observed at about 380 °C. The residue at 500 °C was less than 10% of the initial polymer weight. Figure 9 shows a differential scanning calorimetric (DSC) curve of poly(ADPO). The endothermic peak near 20 °C seems to correspond to a phase transition of the polymer, and the

Table 4. Specific Rotations ($[\alpha]_D$) of ADPO and Poly(ADPO) in Various Solvents

	$[\alpha]_D$	
solvent	poly(ADPO)	ADPO monomer
benzene	−81	−83
toluene	−83	−77
chlorobenzene	−79	−70
THF	−72	−78
DMF	−77	−81
ethyl acetate	−83	−70

Table 5. Solvent Effects on the ADPO Polymerization at 60 °C[a]

solvent	10^5R_p (mol L^{-1} s^{-1})	$10^{-4}M_n$	$[\alpha]_D$
benzene	4.94	1.76	−81
toluene	4.76	1.53	−83
chlorobenzene	5.04	1.75	−79
THF	5.56	0.54	−72
DMF	3.66	1.12	−77
ethyl acetate	3.64	1.47	−83
acetone	4.47	0.79	−80
methanol	2.97	0.72	−81

[a] [ADPO] = 1.08 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}.

large exothermic peak near 350 °C is due to the polymer decomposition.

The homopolymer of ADPO is a white solid and is soluble in THF, chloroform, toluene, benzene, ethyl acetate, *N,N*-dimethylformamide, and chlorobenzene in spite of being a highly isotactic polymer (degree of polymerization = 20−80). On the other hand, it is insoluble in methanol, acetone, acetonitrile, dimethyl sulfoxide, and H_2O. Poly(ADPO) gave a satisfactory elemental analysis.

Some isotactic polymers are well-known to hold a helical structure in a solid state and also in solution.[1−3] When such a polymer holds one-handed helical conformation in a solution, it shows a very large optical rotation due to molecular dissymmetry. Recently poly(phenylacetylene) having an optically active bulky substituent was reported to hold a helical conformation in chloroform and show a much higher specific rotation than that of its monomer.[14] Table 4 shows the values of specific rotation of ADPO and poly(ADPO) in various solvents. Thus, both the monomer and the polymer showed a similar optical rotation in all solvents used, indicating that poly(ADPO) does not hold a stable one-handed helical conformation though the isotactic polymer carries an optically active bulky substituent.

This finding suggests that the low *A* factors for propagation and termination in the ADPO polymerization are not due to the helical conformation of the propagating polymer radical but rather to steric hindrance of the bulky substituent of ADPO and poly(ADPO) radical.

On the other hand, some achiral *N,N*-diarylacrylamides were reported to give optically active polymers by anionic polymerization with optically active initiator, the optical activity of which arises probably from one-handed helicity even in solution.[15]

Solvent Effect on the Polymerization of ADPO with MAIB. The polymerization of ADPO was carried out at 60 °C in several solvents in which poly(ADPO) is soluble except acetone and methanol, because the conformation of the propagating poly(ADPO) radical may depend on the solvent used. The polymerization proceeded apparently homogeneously in acetone, although the isolated poly(ADPO) was no longer soluble in acetone.

Table 5 summarizes the results obtained. Thus, the solvents used were not observed to exert any significant effect on R_p and the optical rotation of polymer formed. Considerably low $\bar{M}_n$ of the polymer formed in THF seems to result from chain transfer to the solvent.[16]

Table 6. Radical Copolymerization of ADPO (M_1) and St (M_2) in Benzene with MAIB at 60 °C[a]

$[M_1]$ in the feed (mol %)	$[M_1]$ in the copolymer (mol %)	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.125	0.163	0.91	1.4
0.250	0.229	1.2	1.4
0.375	0.341	1.2	1.4
0.500	0.414	1.4	1.5
0.625	0.493	1.4	1.5
0.750	0.571	1.4	1.5
0.875	0.685	1.3	1.5

[a] [ADPO] + [St] = 1.08 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}.

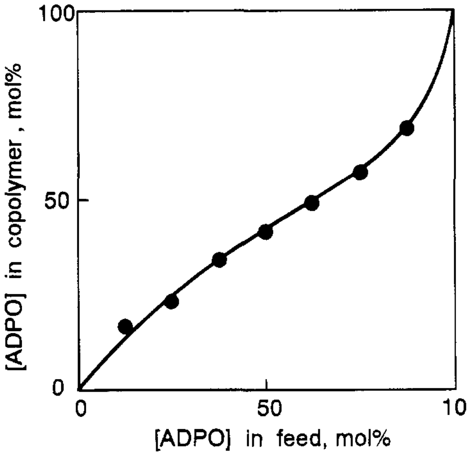


Figure 10. Comonomer−copolymer composition curve for the polymerization of ADPO (M_1) and St (M_2) with MAIB in benzene at 60 °C; the solid line is calculated using r_1 = 0.22 and r_2 = 0.76. [ADPO] + [St] = 1.08 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}.

Table 7. Copolymerization Parameters of Acrylamide Derivatives (M_1) and Styrene (M_2)

acrylamide derivative monomer	r_1	r_2	Q	e	ref
ADPO	0.22	0.76	0.45	0.53	this work
acrylamide	0.58	1.17	0.23	0.54	12
N-octadecylacrylamide	0.54	2.08	0.66	1.64	12
N-methylolacrylamide	0.48	0.03	0.52	1.15	12

These findings also support that poly(ADPO) holds no one-handed helical conformation in solution.

Copolymerization with St. Copolymerization of ADPO (M_1) and St (M_2) with MAIB was carried out at 60 °C. Table 6 summarizes the copolymerization results. The copolymerization yield in each run was less than 10%. The copolymer composition was estimated from the nitrogen content by elemental analysis.

Figure 10 shows the comonomer−copolymer composition curve for the copolymerization of ADPO (M_1) with St (M_2). The monomer reactivity ratios were determined by the curve-fitting method based on a nonlinear least-squares analysis.[17] r_1 = 0.22 and r_2 = 0.76 (SD = 0.01). Using these results, *Q*- and *e*-values of ADPO were calculated to be 0.45 and +0.53, respectively, where Q = 1.0 and e = −0.8 were used for St. The copolymerization parameters of ADPO are compared with those of some acrylamide derivatives in Table 7. Thus, in analogy with other acrylamide derivatives, ADPO was found to be a conjugative and electron-accepting monomer.

The rate constants of cross-propagations in the copolymerization of ADPO and St could be estimated using the k_p values of comonomer and the monomer reactivity

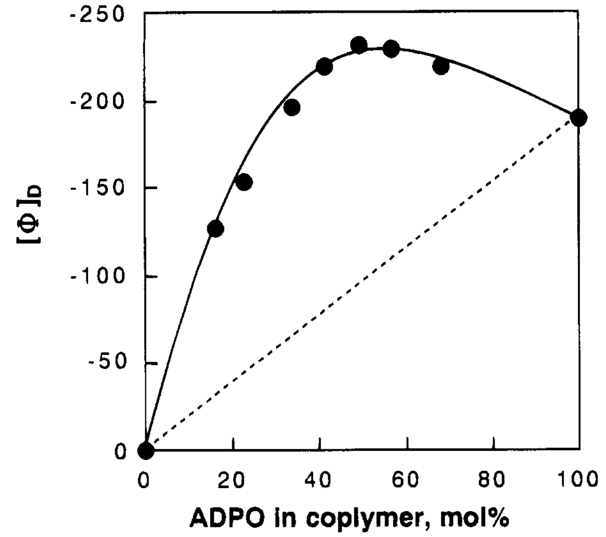


Figure 11. Relationship between molar rotation $[\Phi]_D$ of ADPO with St copolymer and mole fraction of ADPO units in copolymer.

ratios. The rate constants of four propagations in the copolymerization at 60 °C are

$$\sim\mathrm{ADPO}^{\bullet} + \mathrm{ADPO} \xrightarrow{k_{11} = 28\ \mathrm{L\ mol^{-1}\ s^{-1}}} \sim\mathrm{ADPO{-}ADPO}^{\bullet}$$

$$\sim\mathrm{ADPO}^{\bullet} + \mathrm{St} \xrightarrow{k_{12} = 127\ \mathrm{L\ mol^{-1}\ s^{-1}}} \sim\mathrm{ADPO{-}St}^{\bullet}$$

$$\sim\mathrm{St}^{\bullet} + \mathrm{ADPO} \xrightarrow{k_{21} = 383\ \mathrm{L\ mol^{-1}\ s^{-1}}} \sim\mathrm{St{-}ADPO}^{\bullet}$$

$$\sim\mathrm{St}^{\bullet} + \mathrm{St} \xrightarrow{k_{22} = 295\ \mathrm{L\ mol^{-1}\ s^{-1}}\ ^{10}} \sim\mathrm{St{-}St}^{\bullet}$$

Figure 11 shows the relationship between the molar rotation of the copolymer and the mole fraction of ADPO units in the copolymer. Thus, some deviations in the molar rotation were observed from the expected linear relationship. This means that the optical rotation of the copolymer is contributed by any effects other than the optically active substituent of the ADPO unit. The deviation shows a maximum at the mole fraction of the ADPO unit which corresponds to the copolymer of equimolar composition. The values of ($[\Phi]_D - P_2(m_1,m_1)$ $[\Phi m_1,m_1]_D$) were plotted against $P_2(m_1,m_2)$ obtained from the mole fraction of m_1 and the molar rotation of the copolymer, where m_1 and m_2 denote ADPO and St units in the copolymer, and $P_2(m_1,m_1)$ and $P_2(m_1,m_2)$ denote the propabilities of $m_1 - m_1$ and $m_1 - m_2$ diad sequences in the copolymer, respectively. As can be seen from Figure 12, a linear relationship was observed. These findings suggest that the deviation originates from the perturbation of the St unit in the copolymer by the chiral substituent of the ADPO unit.

Conclusion

The polymerization of ADPO, an optically active acrylamide derivative, with MAIB in benzene which is known to give isotactic polymer was found to show conventional kinetic behavior involving bimolecular termination. The homogeneous polymerization system involves an ESR-observable propagating polymer radical. ESR determination of the propagating polymer radical concentration allowed us to estimate the rate constants of propagation (k_p) and termination (k_t). The values of k_p and k_t thus obtained are much lower than those of the usual vinyl monomers including acrylamide. ADPO and its polymer show similar optical rotations in the usual organic solvents, indicating that radically formed poly(ADPO) can not maintain a helical conformation in the solutions. Thus, the extremely low k_p and k_t values are not due to the helical conformation of the propagating polymer radical but rather to the steric hindrance of the bulky substituent.

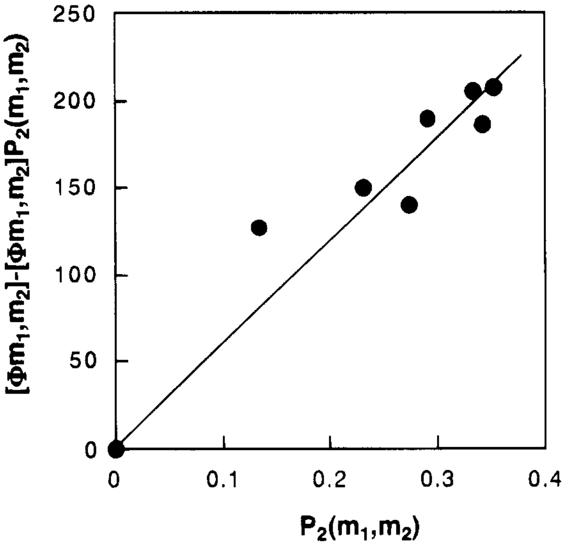


Figure 12. Plot of molar rotation $[\Phi]_D - P_2(m_1,m_1)$ $[\Phi m_1,m_1]_D$ against $P_2(m_1,m_2)$ $[\Phi m_1,m_1]_D$: molar rotation of homopolymer of ADPO. $P_2(m_1,m_1)$, $P_2(m_1,m_2)$: probabilities of $m_1 - m_1$ and $m_1 - m_2$ diad sequences in copolymer.

Copolymerization of ADPO (M_1) and St (M_2) in benzene at 60 °C gave the following copolymerization parameters; $r_1 = 0.22$, $r_2 = 0.76$, $Q_1 = 0.45$, $e_1 = +0.53$. Using k_p of ADPO, r_1 and r_2, the rate constants of cross-propagations were able to be estimated. The resulting copolymer shows the optical rotation arising not only from the chiral substituent of ADPO unit but also from the interaction between ADPO and St units.

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