Polymer Bulletin 35, 345–350 (1995)

Polymer Bulletin

Solvent effects on the radical polymerization of *N*-dodecylmaleimide

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Received: 28 October 1994/Revised version: 27 March 1995/Accepted: 30 March 1995

SUMMARY

The rate of homogeneous polymerization of N-dodecylmaleimide (DMIm) with dimethyl 2,2'-azobisisobutyrate depended significantly on the kind of solvents used. The polymerization systems involved ESR-observable propagating poly(DMIm) radical. The rate constants of propagation(k_p) and termination(k_t) were determined at 50°C in various solvents. The k_p value was smaller in aromatic solvents than in aliphatic ones. The Hammett's plot of k_p against σ-value of the substituents on the aromatic solvents showed that k_p took higher values in the solvents with either electron-accepting or donating substituents. The solvent effects on k_p seemed to stem from complexion of poly(DMIm) radical with solvents.

INTRODUCTION

Considerable attention has been paid to solvents effects on kinetics of the radical polymerization(1-4). It is important for the solvent effects to be discussed on the basis of elementary reactions involved in the radical polymerization. Generally, the initiation and propagation(k_p) rate constants are hardly affected with the kind of solvents, and large variation in the termination rate constant(k_t) with the medium viscosity leads to a noticeable change in the overall polymerization rate(R_p)(5). However, significant solvent effects on k_p have been observed in the radical polymerization of some acrylate monomers(6-12). The solvent effects have been explained in terms of the charge-transfer interaction of propagating polymer radicals with solvent(3,7-10) and of the affinity of propagating polymer chain for solvent(11,12). The charge-transfer interaction is more significant in aromatic solvents than in aliphatic ones(1). The more polar propagating polymer radical interacts more strongly with the aromatic solvents(1,8).

Copolymerization results of maleimide derivatives revealed that their propagating polymer radicals are highly electron-accepting(13-16). Recently some N-substituted maleimides have been found to produce ESR-observable propagating polymer radicals under the actual homogeneous polymerization conditions where the k_p values are able to be determined independently of termination by means of ESR(17-20).

In the present paper we have investigated the solvent effects on the polymerization of N-dodecylmaleimide(DMIm) with dimethyl 2,2'-azobisisoburate(MAIB).

EXPERIMENTAL

DMIm(supplied from Daihachi Chemical Industry Co., Ltd.) was purified by passing its benzene solution through a silica gel column and by recrystallization from ethanol. MAIB was recrystallized from methanol. Solvents were used after

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distillation.

Polymerization was carried out in a degassed and sealed glass tube. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of methanol.

The number- and weight- average molecular weights($\overline{M}_n$ and $\overline{M}_w$) were determined by gel permeation chromatography (GPC) using tetrahydrofuran(THF) as eluent by means of a TOSO-HLC 802A instrument with polystyrene standards for calibration. ESR spectra of the polymerization mixture in a degassed and sealed ESR tube were recorded on a JEOL-JES-FG2XG spectrometer operating at X-band(9.5 GHz) with a TE mode cavity. The radical concentration was estimated by computer double integration of the observed ESR spectra by a calibration with 2,2',6,6'-tetramethylpiperidinyloxy radical (TEMPO) in the same medium.

RESULTS AND DISCUSSION

The polymerization of DMIm with MAIB was performed at 50°C in various solvents, where the concentrations of DMIm and MAIB were 0.500 and 1.00x10^{-2}mol/l, respectively. The eleven solvents used here were benzene, toluene, chlorobenzene, bromobenzene, anisole, methyl benzoate, benzonitrile, ethyl acetate, THF, dioxane and methyl ethyl ketone. The polymerization proceeded homogeneously and the polymer yield(up to about 15%) increased linearly with time without any induction period in all the solvents used.

Table I lists the R_p value and the molecular weight of resulting polymer in each solvent. Thus, R_p and the molecular weight of poly(DMIm) significantly depend on the kind of solvent used. R_p seemed to be higher in the aliphlic solvents than in aromatic ones. The highest R_p in THF was about 5 times the lowest one in benzonitrile. THF and dioxane caused a remarkable decrease in the molecular weight of polymer which is ascribable probably to easy chain transfer to the solvents.

Fig.1 shows ESR spectrum observed in the polymerization of DMIm with MAIB in benzene at 50°C where the concentrations of DMIm and MAIB were 0.500 and 1.00x10^{-2} mol/l, respectively. The spectrum is assignable to the propagating polymer radical of DMIm(I). Similar spectra were observed in the radical polymerization of N-substituted maleimides(17-20). Intensity ratio of the three lines of spectra depends on the kind of N-substituent which might be explicable by superposition of a doublet and a triplet with a 1:2:1 intensity

Table 1. Solvent effects on the polymerization rate(R_P) and the molecular weight of resulting polymer in the polymerization of DMIm(0.50 mol/l) with MAIB(1.00x10^{-2} mol/l) at 50°C.

Solvent	R_Px10^5 (mol/l)	$\overline{M}_n$x10^{-4}	$\overline{M}_w$x10^{-4}	$\overline{M}_w/\overline{M}_n$
Benzene	1.41	9.4	19	2.0
Toluene	1.45	2.4	4.3	1.8
Anisole	1.40	6.3	12	1.9
Chlorobenzene	1.20	4.2	8.5	2.0
Bromobenzene	3.97	12	23	1.9
Methyl benzoate	2.38	12	30	2.5
Benzonitrile	1.10	4.6	8.5	1.8
THF	5.41	0.42	0.55	1.3
Dioxane	3.25	1.6	2.8	1.8
Ethyl acetate	2.83	9.6	19	2.0
Methyl ethyl ketone	1.86	3.1	6.8	2.2

ratio(20). Propagating radicals of the maleimides take probably a pyramidal structure, resulting in the formation of cis- and trans-isomers. The population of these isomers may depend on the bulkiness of substituent. Small peaks were also observed at the both outer sides in Fig.1. These might be due to a different conformation of radical I which is caused by a different structure(cis or trans) of penultimate DMIm unit.

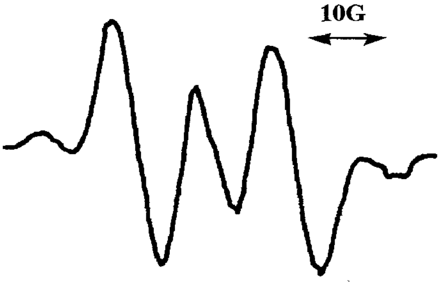


Fig.1 ESR spectrum observed in the polymerization of DMIm(0.50 mol/l) with MAIB($1.00x10^{-2}$ mol/l) in benzene at 50°C.

We have attempted to trap the propagating radical of DMIm with 2-methyl-2-nitrosopropane(BNO). Fig.2 shows ESR spectrum observed for the polymerization system when BNO of a small concentration ($1.2x10^{-3}$mol/l) was added. Thus, each line of the three lines spectrum is futher hyperfine-splitted due to not only α-hydrogen but also β-hydrogen. Such a spectrum is characteristic of a nitroxide formed by trapping a ring radical with BNO(21,22). So, the observed spectrum is assignable to nitroxide radical II formed by trapping propagating radical with BNO. The complicated hyperfine splitting comes from the fact that radical II is possibly a mixture or cis- and trans-isomers. When much lower concentration($2.9x10^{-4}$ mol/l) of BNO was used, a broad spectrum of the same nitroxide was observed without observation of any other nitroxides. These findings support that the spectrum in Fig.1 is due to propagating radical I.

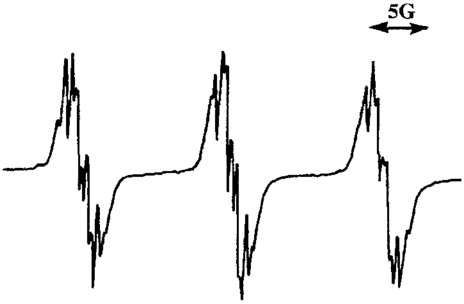
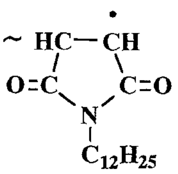
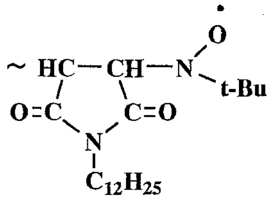


Fig.2 ESR spectrum of the DMIm (0.5mol/l)/MAIB ($1.00x10^{-2}$mol/l)/BNO($1.2x10^{-3}$mol/l) in benzene at 50°C.



(I)



(II)

The ESR spectrum due to the propagating radicals was also observed in all the solvents used except for benzonitrile. The unsuccessful observation of propagating polymer radicals in benzonitrile seems ascribable to a low concentration of polymer radical and high polarity of the solvent which reduces ESR-sensitivity .

Table 2 presents the concentration of poly(DMIm) radical([P•]) determined in the ten solvents by means of ESR. Using R_p and [P•], the k_p values in various solvents were estimated according to equation (1) and are also listed in Table2.

$$R_p = k_p [P\bullet] [DMIm] \quad (1)$$

The obtained k_p values (54 l/mol•sec) of DMIm is similar to that(50 l/mol•s) of N-cyclohexylmaleimide at 50°C in benzene(17). As can be seen from the table, k_p depended considerably on the solvent used. The largest k_p observed in THF was

Table 2. Polymer radical concentration([P•]), k_p, k_d f and k_t in the polymerization of DMIm(0.50 mol/l) with MAIB(1.00x10^{-2} mol/l) at 50°C in various solvents.

Solvent	[P•]x10^7 (mol/l)	k_P (l/mol•s)	k_d fx10^6 (s^{-1})	k_tx10^{-5} (l/mol•s)	η (30°C) (cP)
Benzene	5.2	54	1.57	1.2	0.564
Toluene	2.8	104	1.76	4.5	0.522
Anisole	1.6	175	1.32	10	0.901
Chlorobenzene	3.0	80	1.78	4.0	0.715
Bromobenzene	6.2	128	1.23	0.64	1.00
Methyl benzoate	3.2	149	0.88	1.7	1.673
THF	2.8	386	--	--	--
Dioxane	2.6	250	--	--	--
Ethyl acetate	2.4	235	1.58	5.5	0.400
Methyl ethyl ketone	1.9	196	--	--	--

about 7 times the smallest one in benzene. The k_p value showed a tendency to be lower in the aromatic solvents than in the aliphatic ones. This finding strongly suggests that the solvent effects on the propagation stem from complexation of poly(DMIm) radical with solvent(1).

Further, the k_p values even in the aromatic solvents were fairly different from each other. The highest k_p in anisole was about three times the lowest one in benzene. Fig.3 shows the Hammett's plot of k_p value for DMIm against σ–value of the substituent on the aromatic solvents. Thus, k_p took higher values in the solvents with either electron-accepting or electron-donating substituents. Such a tendency was also reported to be observed for methyl and phenyl methacrylates as shown in Fig.2(7,8). Kamachi et al explained the solvent effect in terms of formation of an electron donor-acceptor complex between the propagating polymer radical and solvent and correlated it with the delocalization stabilization for the complex formation(7-9). Evidently from Fig.2, the aromatic solvents exerted fairly larger effect on k_p (50°C) for DMIm than on those(30°C) for the mathacrylates, indicating that the solvents interact more effectively with the propagating polymer radical of DMIm than with those of the methacrylates. This is because the propagating end of poly(DMIm) radical is highly electron-accepting radical on a nearly planar five-membered ring(13-16).

We have also attempted to determine the k_t value for DMIm at 50°C in several solvents. The k_df value of MAIB under the polymerization conditions was determined by means of radical trapping with

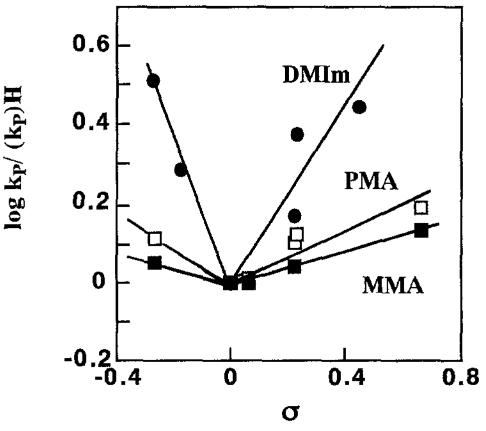


Fig.3 Hammett's plot of solvent effect on k_P for DMIm (50°C), methyl methacrylate (MMA) and phenyl methacrylate(PMA) (30°C).

TEMPO in the same manner as described in the previous papers (18,23), where k_d is the rate constant of decomposition of MAIB and f is the initiator efficiency. MAIB decomposes into 1-methyl-1-methoxy-cabonylethyl radicals and nitrogen. Some of the primary radicals disappear through the cage reactions. The others diffuse through the solvent cage to initiate the polymerization of DMIm. When the decomposition of MAIB is conducted in the presence of TEMPO, the solvent cage-escaping primary radicals are trapped with TEMPO to yield a coupling product. The decrease in the TEMPO concentration was followed by ESR. Fig.4 shows a typical plot of TEMPO concentration against the reaction time in toluene at 50°C. From the slope of the straight line, the $k_d f$ value was evaluated. Futher using the polymer radical concentration and $k_d f$ value, the k_t value was calculated according to equation(2).

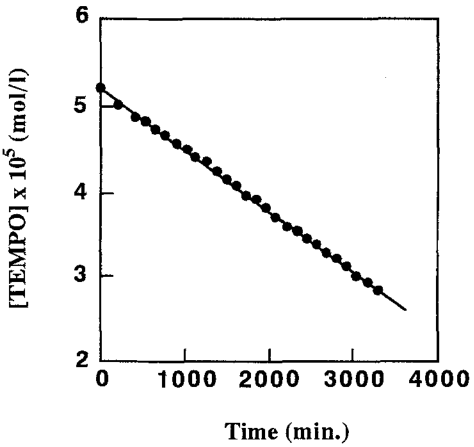


Fig.4 Relationship between time and [TEMPO] in the polymerization of DMIm(0.500 mol/l) with MAIB(2.00×10^{-3} mol/l) at 50°C in toluene in the presence of TEMPO(5.19×10^{-5} mol/l)

$$2k_d f[\mathrm{MAIB}] = k_t [\mathrm{P}\bullet]^2 \quad (2)$$

Table.2 summaizes the results obtained in seven solvents. The table also lists the viscosity(30°C) of solvents used. Thus, the k_t value showed a tendency to be smaller in the more viscous solvent though k_t in anisole was much higher than expected. At present we do not have any reasonable explanation for such a high k_t value in anisole, a fairly viscous solvent.

Matsumoto et al found that the k_t values from the stationary concentrations of radicals observed in the polymerizations of N-substituted maleimides are consistent with these from decay-profiles of the radicals(20). The R_p values estimated by using the $k_d f$, k_p and k_t values obtained here are quite consistent with those in Table 1. These results also support that the spectrum in Fig.1 is due to propagating radical I.

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