A Kinetic Study on Polymerization of Methyl Methacrylate with Di-*t*-Butyl Perfumarate

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ABSTRACT: Di-*t*-butyl perfumarate (DBPF) was found to induce the radical polymerizations of various vinyl monomers at 60°C in benzene, although the initiation activity was considerably lower than those of dimethyl 2,2′-azobisisobutyrate and benzoyl peroxide. The polymerizations with DBPF showed a tendency of dead-end polymerization. The polymerization of methyl methacrylate (MMA) with DBPF was kinetically studied in chlorobenzene. The initial polymerization rate (R_p) was given by $R_p = k$ [DBPF]$^{0.5}$ [MMA]$^{1.1}$. The overall activation energy of the polymerization was 47 kJ/mol, a very low value. Use of this value and activation energies of propagation and termination for MMA gave an unexpectedly low activation energy (65 kJ/mol) to the decomposition of DBPF, a *t*-butyl perester, in the polymerization system. An ESR study on the polymerization of di-2-ethylhexyl itaconate with DBPF revealed that the observed dead-end tendency comes from the consumption of DBPF. These results suggest that the initiator efficiency of DBPF is considerably low in the present polymerization systems. Some solvent effect was observed on the polymerization of MMA with DBPF. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 218–224, 2000

Key words: radical polymerization; radical initiator; di-*t*-butyl perfumarate; ESR spectrum

INTRODUCTION

Various peroxide compounds, including diacyl peroxides, acyl peresters, dialkyl peroxides and alkyl hydroperoxides, have served as radical initiators for the vinyl polymerization.[1] Some workers have been interested in acrylate- and styrene-type monomers carrying the peroxy bond, which can act as a monomer and initiator.[2–4] Homo- and copolymers from such monomers were used as polymer initiators to prepare graft copolymers.

Recently, *t*-alkyl permethacrylates[3] and related monomers[5–8] have been observed to serve as chain transfer reagents via an addition–substitution mechanism.

Our attention has been denoted to di-*t*-butyl perfumarate (DBPF), which is a congested 1,2-disubstituted monomer with two peroxyester groups. Few kinetic studies have been performed on the vinyl polymerization with DBPF, although it was already reported that DBPF was radically homo- and copolymerizable and its copolymers were used for preparations of graft copolymers and long-lived propagating polymer radicals.[9–11] So, we have kinetically examined the polymerization of methyl methacrylate (MMA) initiated with DBPF.

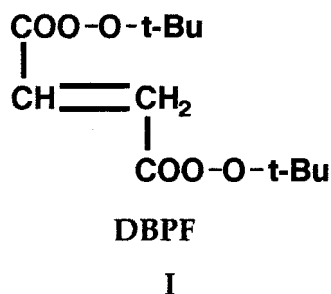The present paper describes kinetic results observed in the polymerization of MMA with DBPF (**I**):

COO-O-t-Bu
|
CH====CH₂
|
COO-O-t-Bu

DBPF

I

EXPERIMENTAL

Materials

DBPF was prepared by the reaction of fumaroyl chloride with sodium per-*t*-butoxide in dichloromethane in an ice bath.[10] DBPF was purified as a white crystal by recrystallization from a methanol–water mixture and identified by IR, ^{1}H-NMR, and elemental analysis (Mp 30°C).

Dimethyl 2,2′-azobisisobutyrate (MAIB) was recrystallized from methanol. Benzoyl peroxide (BPO) was reprecipitated by pouring its chloroform solution (20 mL) into methanol (50 mL). MMA, butyl acrylate (BA), styrene (St), di-2-ethylhexyl itaconate (DEHI), and vinyl acetate (VAc) were freed from inhibitor by washing with a 5% NaOH aqueous solution, dried over sodium sulfate, and distilled before use. Acrylonitrile (AN) and solvents were used after distillations.

Polymerizations

Polymerizations of vinyl monomers were conducted in a degassed and sealed glass tube for a given time under shaking. The resulting polymers were isolated by pouring the polymerization mixtures into a large amount of methanol (MMA, BA, St, and DEHI) or *n*-haxane (VAc), filtered, dried in a vacuum, and weighed. No formation of polymers with low molecular weights (MMA, BA, St, DEHI) was confirmed by using a methanol–water mixture as precipitant.

Measurements

^{1}H-NMR spectrum was obtained with a Hitachi R-24 (60 MHz) spectrometer. IR spectrum was obtained with a Perkin-Elmer 1600 FT-IR spectrometer. Gel permeation chromatograms (GPC) were recorded at 38°C by a TOSO-HLC 802 instrument with tetrahydrofuran (THF) as carrier. From the GPC results, the number-average ($\bar{M}_n$)

and weight-average ($\bar{M}_w$) molecular weights of the polymers were determined with calibration with poly(St) standards. ESR spectrum of the polymerization mixture of DEHI in a degassed and sealed ESR tube was recorded on a JEOL-JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity. The concentration of polymer radical was determined by double integration of the observed ESR spectrum, where 2,2,6,6-tetramethylpiperidinyloxyl radical (TEMPO) in the same medium (benzene solution of DEHI) was used as standard.

RESULTS AND DISCUSSION

Polymerization of Some Vinyl Monomers with DBPF

Figure 1 compares the initiation activity of DBPF with those of MAIB and BPO, conventional radical initiators, using MMA as monomer in benzene at 60°C, where the concentrations of monomer and initiator were 4.67 and 5.00 × 10^{-3} mol/L, respectively. Thus, DBPF showed fairly lower initiation activity compared to those of BPO and MAIB. It is noteworthy that the polymerization with DBPF shows a tendency of dead-end polymerization.[12]
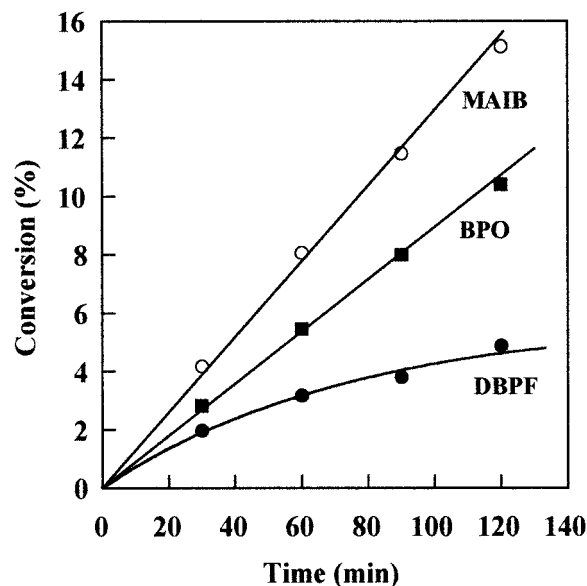

Figure 1 Time–conversion curves for the polymerization of MMA with MAIB, BPO, and DBPF at 60°C in benzene: [initiator] = 5.00 × 10^{-3} mol/L; [MMA] = 4.67 mol/L.
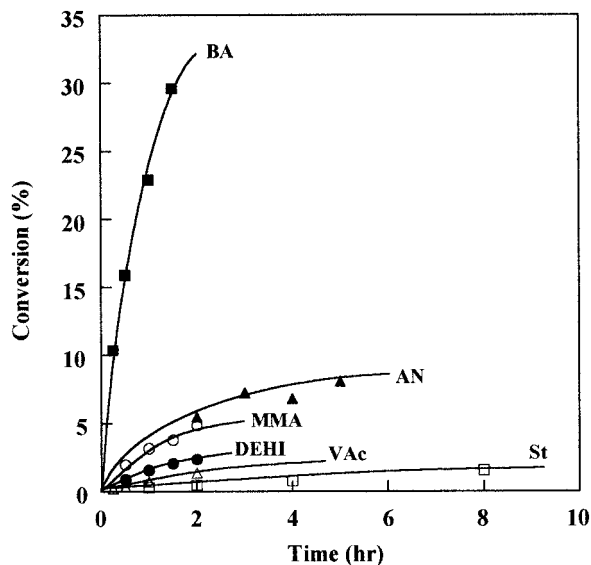
Figure 2 Time–conversion curves for the polymerizations of various monomers with DBPF at 60°C in benzene: [DBPF] = 5.00×10^{-3} mol/L, monomer: 2 mL; benzene: 2 mL.

Figure 2 shows the results observed when several vinyl monomers were polymerized with DBPF in benzene at 60°C. The monomers used were MMA, BA, AN, DEHI, St, and VAc. DBPF was observed to induce all the polymerizations of the monomers used. Most of the polymerization systems again tended to show a dead-end polymerization behavior. The initiation activity of DBPF for the monomers decreases in the following order: BA, AN, MMA, DEHI, VAc, and St. This order is similar to that expected from $k_p/(k_t^{1/2})$ values reported for the monomers, where k_p and k_t are the rate constants of propagation and termination.[13]

Table I summarizes the molecular weights of resulting polymers compared with those of poly(MMA) and poly(VAc) separately prepared with MAIB of the same concentration. The molecular weights of poly(MMA)s are comparable, whereas the molecular weight of poly(VAc) with DBPF is much lower than that of poly(VAc) with MAIB. This suggests that DBPF acts not only as initiator but also as a chain transfer reagent in the VAc polymerization.[3]

Kinetic Study on the Polymerization of MMA with DBPF

The polymerization of MMA with DBPF was kinetically studied in chlorobenzene.

Figure 3 illustrates the time-conversion curves observed in the temperature range of 50–80°C, where the concentrations of MMA and DBPF were 4.67 and 5.00×10^{-3} mol/L, respectively. Thus, a dead-end tendency was observed in the polymerization at each temperature. Figure 4 presents the Arrhenius plot of the initial polymerization rate (R_p) obtained from the curves in Figure 3. The overall activation energy of the polymerization was estimated to be 47 kJ/mol being a very low value compared to that (84 kJ/mol) of the MMA polymerization with 2,2′-azobisisobutyronitrile.[14]

Figure 5(a) shows the relationship between R_p and the DBPF concentration observed at 60°C at a fixed MMA concentration of 4.67 mol/L. R_p was found to increase in proportion to the 0.5 power of the initiator concentration. Figure 5(b) shows the effect of monomer concentration on R_p at 60°C when the MMA concentration was changed, keeping the DBPF concentration constant at 5.00

Table I   Polymerization of Various Vinyl Monomers with DBPF at 60°C in Benzene

Monomer (M)	Concentration [M] (mol/L)	Conversion (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
MMA	4.67	1.98	6.00×10^5	2.19
		(4.18)	(2.34×10^5)	(1.96)
St	4.36	1.55	4.18×10^4	1.98
VAc	5.41	0.73	3.18×10^3	1.57
		(6.61)	(1.24×10^5)	(1.86)
BA	5.31	10.40	7.97×10^5	2.68
DEHI	1.33	1.56	1.92×10^4	1.64
AN	7.60	—	—	—

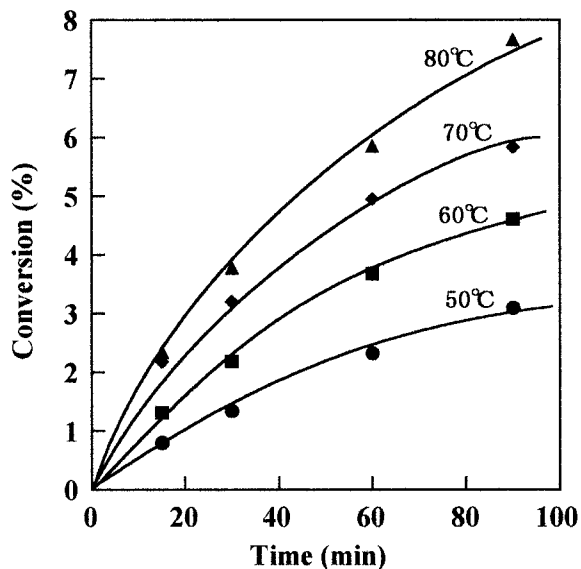Values are for [DBPF] = 5.0×10^{-3} mol/L; values in parentheses are for [MAIB] = 5.0×10^{-3} mol/L.

Figure 3 Time–conversion curves for the polymerization of MMA with DBPF at different temperatures in chlorobenzene: [DBPF] = 5.00×10^{-3} mol/L; [MMA] = 4.67 mol/L.

Figure 4 Temperature effect on the polymerization rate (R_p).

$\times$ 10^{-3} mol/L. R_p was proportional to the 1.1 power of the monomer concentration.

From the above results, R_p was given by the following equation:

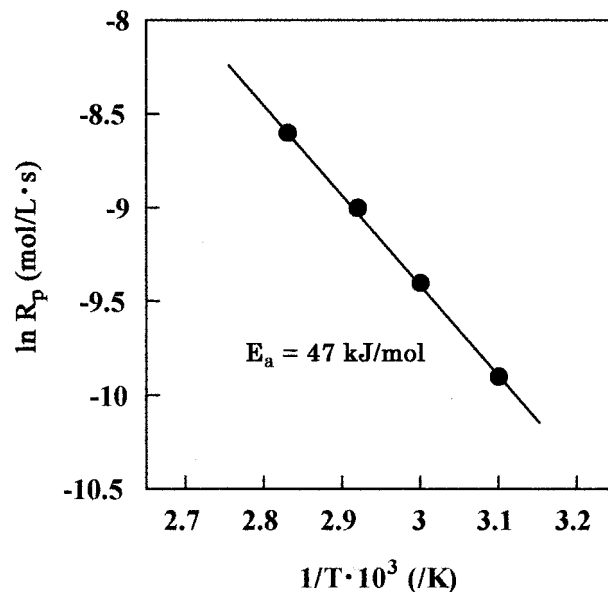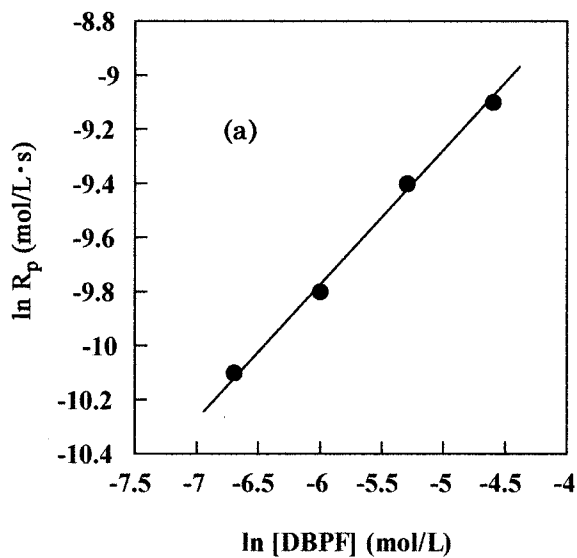$$R_p = k[\text{DBPF}]^{0.5}[\text{MMA}]^{1.1} \qquad (1)$$

Thus, the present polymerization was found to proceed through the conventional radical polymerization mechanism involving bimolecular termination.

In the conventional radical polymerization, the overall activation energy (E_a) of the polymerization is related to the activation energies of initi-
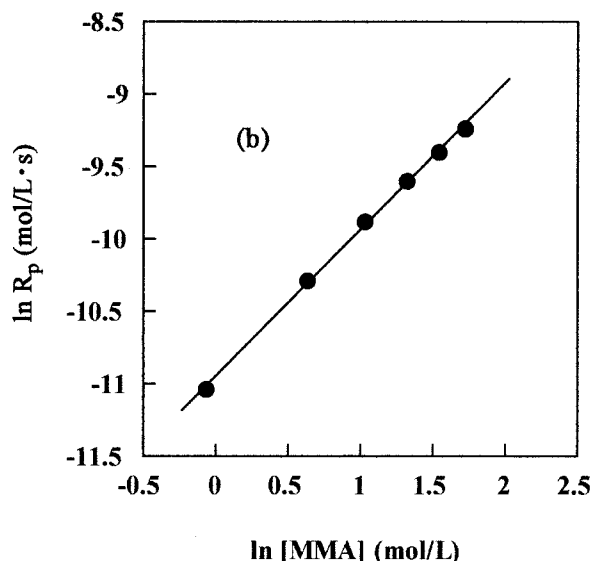

Figure 5 Dependence of the polymerization rate (R_p) on the (a) initiator and (b) monomer concentrations at 60°C in chlorobenzene: (a) [MMA] = 4.67 mol/L; (b) [DBPF] = 5.00×10^{-3} mol/L.

Table II   Molecular Weights and Molecular Weight Distribution of Poly(MMA)s Obtained in the Polymerization of MMA with DBPF in Chlorobenzene

[DBPF] = 10^3 (mol/L)	[MMA] (mol/L)	Temp. (°C)	Conv. (%)	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
5.0	4.67	50	3.10	7.66	1.69	2.2
5.0	4.67	60	1.31	5.52	1.38	2.5
5.0	4.67	70	3.20	5.07	1.18	2.3
5.0	4.67	80	7.66	4.69	1.41	3.0
1.25	4.67	60	1.40	9.96	2.19	2.2
2.5	4.67	60	1.82	7.92	1.74	2.2
10.0	4.67	60	1.91	3.81	0.95	2.5
5.0	0.94	60	2.35	1.54	0.29	1.9
5.0	1.87	60	2.31	2.87	0.60	2.1
5.0	2.81	60	2.40	3.93	0.83	2.1
5.0	3.74	60	3.45	4.24	0.93	2.2
5.0	5.61	60	2.43	6.50	1.43	2.2

ator decomposition (E_d), propagation (E_p), and termination (E_t) by eq. (2):

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

Using $E_p = 20$ and $E_t = 12$ kJ/mol reported for MMA[15] and $E_a = 47$ kJ/mol (Fig. 4), $E_d = 65$ kJ/mol was estimated for DBPF in the present polymerization. This E_d value is much lower than those of t-butyl perpivalate (113 kJ/mol)[16] and t-butyl perbenzoate (137 kJ/mol).[17] Table II summarizes the molecular weights of poly(MMA)s formed under different polymerization conditions. The molecular weight decreases with increasing initiator concentration, with decreasing monomer concentration, and with rising temperature. Such behaviors are similar to those of conventional radical polymerization.

Figure 6 shows the relationship between R_p and the reciprocal of degree of polymerization (DP) of poly(MMA) observed when the DBPF concentration was varied at a fixed MMA concentration at 60°C. A linear relationship observed here excludes any significant chain transfer to the initiator in the present polymerization of MMA with DBPF. This is compatible with the fact that dialkyl fumarate is not incorporated in the resulting polymers in the copolymerization with MMA,[18] leading to no expectation that DBPF acts as chain transfer of addition–substitution type in the MMA polymerization.

Figure 6   Relationship between degree of polymerization ($\overline{DP}$) and the polymerization rate (R_p) at 60°C in chlorobenzene.

ESR Study on the Polymerization of DEHI with DBPF

As mentioned above, a dead-end tendency was observed in the vinyl polymerization with DBPF. In order to clarify the reason for this phenomenon, the polymerization of DEHI with DBPF was examined by means of ESR since DEHI is reported to yield ESR-observable propagating polymer radical (**II**) under the actual polymerization conditions.[19]
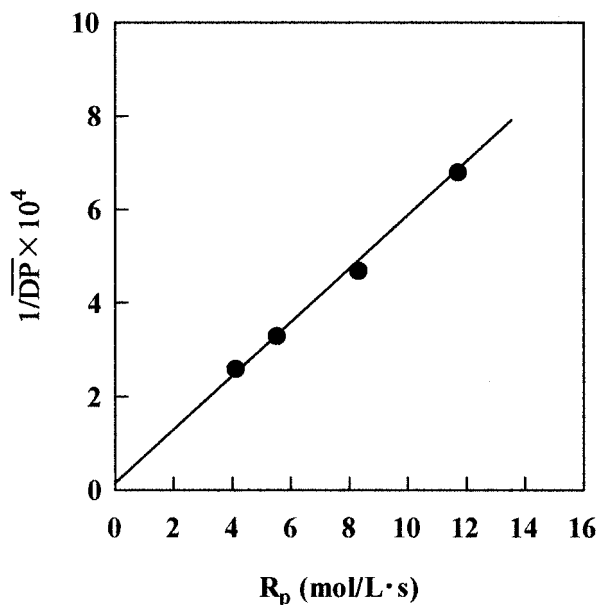
$$C_2H_5$$

$$|$$

$$CH_2COO{\cdot}CH_2CHC_4H_9$$

$$\sim\sim\sim CH_2{-}C\cdot$$

$$COO{\cdot}CH_2CHC_4H_9$$
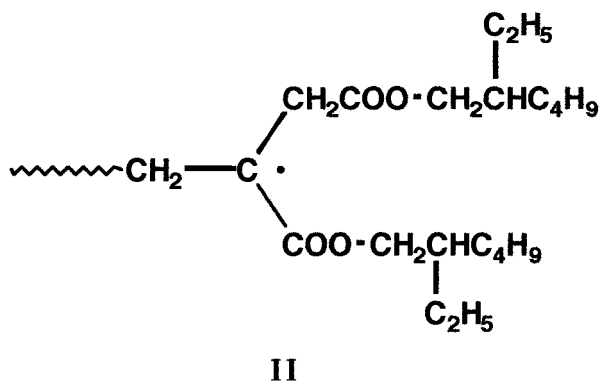
$$|$$

$$C_2H_5$$

II

Figure 7 shows ESR spectra observed in the polymerization of DEHI (1.33 mol/L) with DBPF (5.00×10^{-3} mol/L) at 60°C in benzene. The observed five-line spectrum is assignable to the propagating poly(DEHI) radical (**II**). Thus, the spectrum intensity, that is, the polymer radical concentration, was found to decrease with time.

Figure 8(a) shows the plot of the ESR-determined polymer radical concentration ([$P\cdot$]) against time. The polymer radical concentration decreased gradually with time. As can be seen from
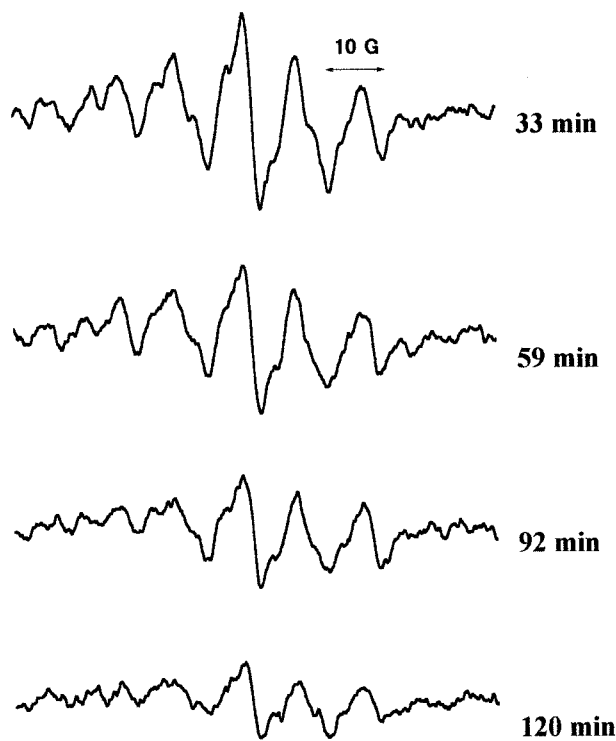

Figure 7 ESR spectral change observed in the polymerization of DEHI with DBPF at 60°C in benzene: [DBPF] = 5.00×10^{-3} mol/L; [DEHI] = 1.33 mol/L.
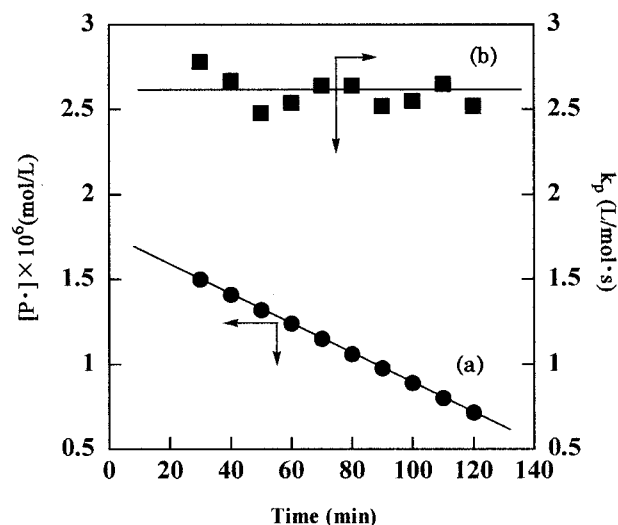

Figure 8 Relations of (a) poly(DEHI) radical concentration ([$P\cdot$]) and (b) propagation rate constant (k_p) with time in the polymerization of DEHI with DBPF at 60°C in benzene: [DBPF] = 5.00×10^{-3} mol/L; [DEHI] = 1.33 mol/L.

Figure 8(b), however, the k_p value was almost constant independently of time. The k_p values were estimated according to eq. (3), where R_{ins} is the instantaneous polymerization rate obtained from the time-conversion curve:

$$R_{ins} = k_p[P\cdot][DEHI] \qquad (3)$$

The k_p value estimated here is closely similar to that (2.3 L/mol s^{-1}) separately obtained in the polymerization of DEHI with MAIB in benzene at 60°C. These findings indicate that the above observed dead-end tendency comes from consumption of DBPF. As shown in Figure 1, however, the initiation activity of DBPF is rather lower compared to that of MAIB or BPO, in spite of faster consumption of DBPF. Since it is unlikely for DBPF to be consumed through chain transfer reaction (Fig. 6), DBPF may decompose not only via radical but also ionic mechanism, leading to a low initiator efficiency.

Solvent Effect on the Polymerization of MMA with DBPF

The above-mentioned results suggest that the DBPF decomposition involves complexed mechanisms in the polymerization system. Some fluorinated peroxides, being strongly electron-accept-
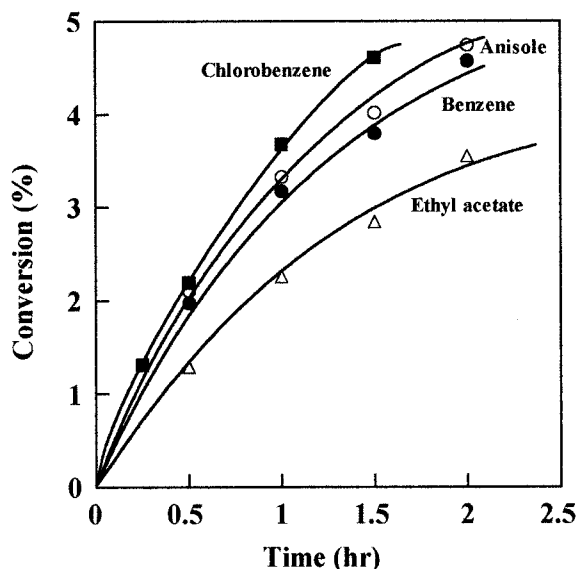
Figure 9 Time–conversion curves for the polymerization of MMA with DBPF at 60°C in different solvents: [DBPF] = 5.00×10^{-3} mol/L; [MMA] = 4.67 mol/L.

ing, are reported to undergo electron-transfer reactions with aromatic compounds as well as homolysis of peroxide bonds.[20] It is possible that DBPF, a strong electron acceptor, also decomposes partially via electron-transfer mechanism.

Such a possibility leads us to examine the solvent effect on the polymerization of MMA with DBPF. Figure 9 shows the polymerization results obtained at 60°C in different solvents. Thus, aromatic solvents were found to accelerate the polymerization compared to ethyl acetate. However, the substituents on the benzene ring seemed to exert little effect. The resulting poly(MMA)s showed similar molecular weights ($\bar{M}_n$ = 6–8 $\times 10^5$). Further efforts are required to elucidate the decomposition mechanism of DBPF.

CONCLUSION

DBPF induces the radical polymerizations of vinyl monomers at 60°C in benzene, although the initiation activity is lower than those of MAIB and BPO. The vinyl polymerization with DBPF shows a tendency of dead-end polymerization. The initial rate of MMA polymerization with DBPF in chlorobenzene at 60°C obeys the ideal kinetics of radical polymerization. The overall activation energy of polymerization is very low, 47 kJ/mol. From an ESR study on the polymerization of DEHI with DBPF, the observed dead-end tendency is found to come from the fast consumption of DBPF in the polymerization system, indicating a low initiator efficiency.

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