Polymer Journal, Vol. 11, No. 4, pp 267—271 (1979)

Vinyl Polymerization. CCCLXXVI. Polymerization of 2,2-Dimethyl-3-oxobutyl Methacrylate*

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(Received April 19, 1978)

ABSTRACT: 2,2-Dimethyl-3-oxobutyl methacrylate (DMBM) was synthesized from 4-hydroxy-3,3-dimethyl-2-butanone and methacrylic acid. The polymerization of DMBM was carried out in benzene at 60°C, using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The rate equation was found to be usual: $R_p = k[\mathrm{AIBN}]^{0.58}\ [\mathrm{DMBM}]^{0.98}$. The polymerization parameters (E_a, $k_p/k_d^{1/2}$, $2fk_d$, C_m, and C_s) were also determined. From the copolymerization with styrene, the reactivity ratios, Q and e of DMBM were obtained. It is also proposed that the values of Q and e of any vinyl monomers could be calculated from the $\lambda_{\max}$ value of the UV spectrum and the chemical shift of the β-carbon atom of the vinyl group in the ^{13}C-NMR spectrum of the monomer.

KEY WORDS 2,2-Dimethyl-3-oxo-butyl Methacrylate / Kinetic Equation / Kinetic Constant / Monomer Reactivity Ratio / Q, e-Values /

In our series of studies on the syntheses of photodegradable plastics, we reported the polymerization of 2,2,4-trimethyl-3-oxopentyl methacrylate (TMPM) in a previous paper.[1]

In a present paper, 2,2-dimethyl-3-oxobutyl methacrylate (DMBM) was prepared by the reaction of 4-hydroxy-3,3-dimethyl-2-butanone (1-ML-MIPK) with methacrylic acid. The homopolymerization of DMBM and the copolymerization with styrene (St) were investigated. The kinetic parameters of DMBM were also compared with those of TMPM.

EXPERIMENTAL

Materials

Preparation of 4-Hydroxy-3,3-dimethyl-2-butanone (1-ML-MIPK). A mixture of 450 cm^3 of 37-% formaline, 389 g of isopropyl methyl ketone, 100 cm^3 of *1-N* NaOH, and 900cm^3 of methanol was refluxed for 20 h. By repeated distillation, 1-ML-MIPK was isolated: yield 236 g, bp 84.5—86°C/16 mmHg.

Preparation of DMBM. Fifty cm^3 of 1-ML-MIPK and 50 cm^3 of methacrylic acid were added into 300 cm^3 of benzene containing 1.0 cm^3 of conc. sulfuric acid and 0.1 g of *p*-benzoquinone. The mixture was refluxed for 10.5 h, and water which was generated during the reaction was removed. The resulting benzene solution was washed with an aqueous solution of sodium bicarbonate. After the evaporation of the benzene, the residue was fractionated under vacuum in a stream of nitrogen. DMBM was obtained as a colorless liquid in a yield of 60 g (77%); bp 79—80°C (3 mmHg), n_D^{30} 1.4438, d^{20} 0.9845, d^{30} 0.9800; IR (NaCl) 1633 ($\nu_{C=C}$) and 1710 cm^{-1} ($\nu_{C=O}$); $\lambda_{\max}$ 219.7 nm, $\varepsilon_{\max}$ 3224 (in ethanol at 20°C). ^{1}H NMR is shown in Figure 1. ^{13}C NMR** (CDCl$_3$) 210.4 (Cⓓ), 166.6 (Cⓗ), 136.0 (Cⓘ), 125.6 (Cⓐ), 70.1 (Cⓕ), 47.8 (Cⓔ), 25.3 (Cⓘ), 21.7 (Cⓖ), 18.2 (Cⓑ). *Anal.* Calcd for C$_{10}$H$_{16}$O$_3$: C, 65.19%,

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[*] Vinyl Polymerization. 375: Y. Nakamura, T. Ouchi, and M. Imoto, *Bull. Chem. Soc. Jpn.*, **51**, 3574 (1978).

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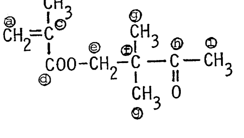


$CH_2=C(CH_3)-COO-CH_2-C(CH_3)_2-C(=O)-CH_3$

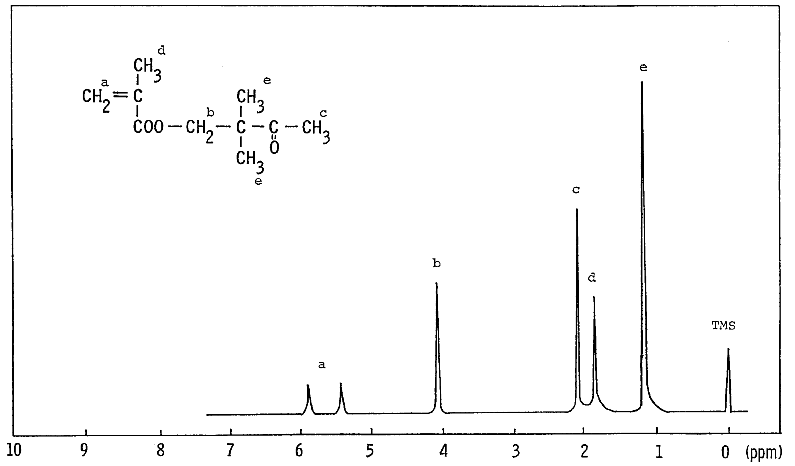
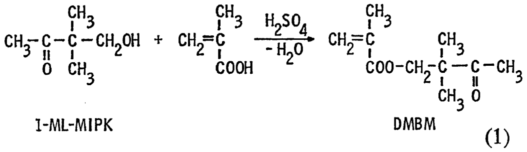


Figure 1. ^{1}H-NMR spectrum (100 MHZ) of DMBM: reference, TMS; solvent, CCl_4.

H, 8.75%. Found: C, 65.07%, H, 8.96%.



$$CH_3-\underset{\|}{\overset{}{C}}(=O)-C(CH_3)_2-CH_2OH + CH_2=C(CH_3)COOH \xrightarrow[-H_2O]{H_2SO_4} CH_2=C(CH_3)COO-CH_2-C(CH_3)_2-C(=O)-CH_3 \quad (1)$$

Other Reagents. Monomers were purified by successive washings with aqueous solutions of sodium thiosulphate and sodium hydroxide and were distilled twice just before the polymerization. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized three times from methanol. Benzene was purified by the conventional method.

Procedures

A glass ampoule was charged with the prescribed amounts of monomer, AIBN, and benzene. The ampoule was then sealed under vacuum after thawing with nitrogen. The tube was heated in the dark in a thermostat without shaking. The contents were poured into a large amount of petroleum ether to precipitate the polymer, which was dried *in vacuo* to a constant weight.

The polymer of DMBM obtained was white. *Anal.* Calcd for $(C_{10}H_{16}O_3)_n$: C, 65.19%, H, 8.75%. Found: C, 64.72%, H, 8.77%.

Moreover, the absorptions of the vinyl group at 1633 and 910 cm^{-1} assigned to νC=C and δCH were recognized in the IR spectrum of the monomer but not in that of the polymer.

The number-averaged molecular weight ($\bar{M}_n$) of the polymer of DMBM was measured osmometrically at 30°C in benzene, using a Mechrolab Dynamic Osmometer 501 (Yokogawa—Hewlett Packard).

From the plots shown in Figure 2, the following equation was obtained.

$$[\eta]^{30^\circ C}_{\text{benzene}} = 1.45 \times 10^{-4} \bar{M}_n^{0.63} \qquad (2)$$

The composition of the copolymer was determined by the elemental analyses of C and H.

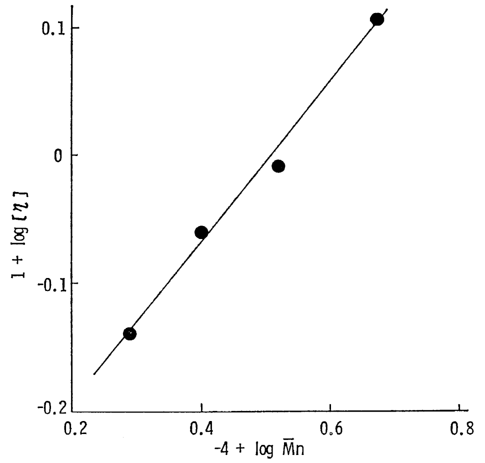


Figure 2. Plots of log [η] *vs.* log $\bar{M}_n$; solvent, benzene; temp, 30°C.

RESULTS AND DISCUSSION

Homopolymerization of DMBM

Rate Equation. The reaction orders of DMBM and AIBN were determined from the results shown in Figure 3. The rate of polymerization, R_p, can be expressed as follows.

$$R_p = k[\mathrm{AIBN}]^{0.58}[\mathrm{DMBM}]^{0.98} \qquad (3)$$

Accordingly, the following general rate equation can be set up.

$$R_p = k[\mathrm{AIBN}]^{1/2}[\mathrm{DMBM}] \qquad (4)$$

Activation Energy. The polymerizations of DMBM were carried out at 55—70°C. The time—conversion curves shown in Figure 4 were obtained. As been clear in this figure, there are good linear relationships and no induction period. Therefore, from the slopes of the straight lines, the rates of polymerization could be calculated.

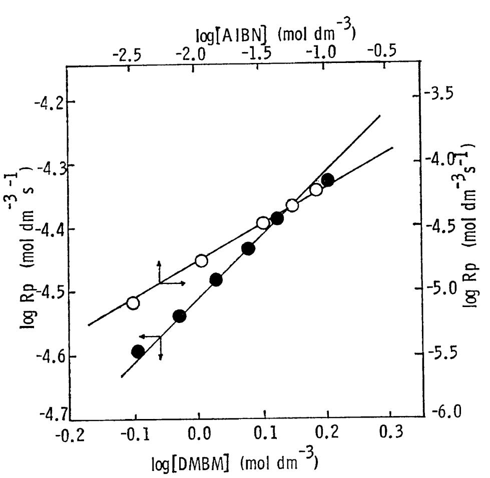


Figure 3. Dependence of the rate of polymerization on the concentrations of AIBN and DMBM: ●, [AIBN]=3.32×10^{-2} mol dm^{-3}, [DMBM]=8.02×10^{-1}∼1.61 mol dm^{-3}; ○, [AIBN]=3.28×10^{-3}∼8.86×10^{-2} mol dm^{-3}, [DMBM]=1.07 mol dm^{-3}; solvent, benzene; temp, 60°C.

Using the values of the rate constants which were calculated by eq 4 from the experimental rates, Arrhenius plots were made. The overall activation energy was calculated to be 108 kJ mol^{-1}. This value is almost equal to the TMPM value,[1] 110 kJ mol^{-1}.

Determination of Kinetic Constants. In order to estimate the various kinetic constants, the polymerizations which gave the results shown in Figure 5 were carried out.

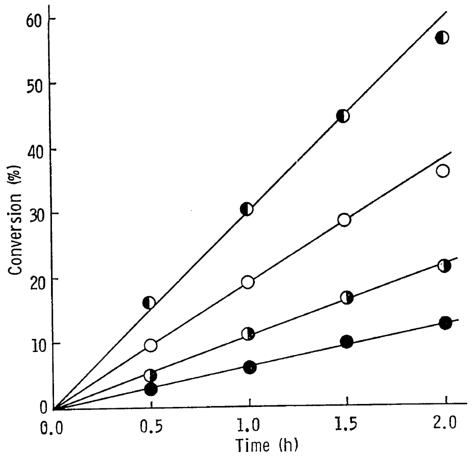


Figure 4. Plots of conversion of DMBM *vs.* time: [DMBM], 1.07 mol dm^{-3}, [AIBN]=3.32×10^{-2} mol dm^{-3}; solvent, benzene; ●, 55°C; ◑, 60°C; ○, 65°C; ◐, 70°C.

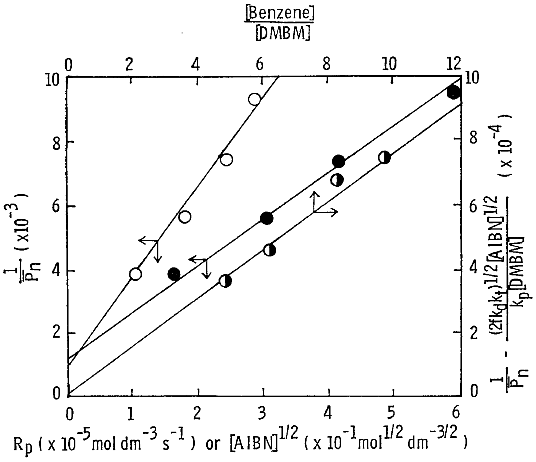


Figure 5. Determination of kinetic constants*: ●, $1/\bar{P}_n$ *vs.* R_p, [DMBM]=1.07 mol dm^{-3}, [AIBN]=1.11×10^{-2}∼8.86×10^{-2} mol dm^{-3}; ○, $1/\bar{P}_n$ *vs.* R_p *vs.* [AIBN]$^{1/2}$, [DMBM]=1.07 mol dm^{-3}, [AIBN]=1.11×10^{-2}∼8.86×10^{-2} mol dm^{-3}; ◑, $\{1/\bar{P}_n - 2(fk_dk_t)^{1/2}[\mathrm{AIBN}]^{1/2}/k_p[\mathrm{DMBM}]\}$ *vs.* [Benzene] / [DMBM], [DMBM]=0.935∼1.60 mol dm^{-3}, [AIBN]=3.32×10^{-2} mol dm^{-3}; solvent, benzene; temp, 60°C.

* C_m and C_s are the chain transfer constants to monomer and solvent; [M] and [S] are the concentrations of monomer and solvent; f is an initiator efficiency; k_d, k_p, and k_t are the the rate constants for decomposition of initiator, propagation, and termination, respectively.

From the results obtained in Figure 5, the kinetic constants listed in Table I were calculated;[6] they are compared with those of TMPM.

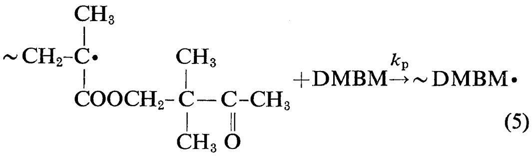
Table I. Kinetic constants[a]

Monomer	$k_p/k_t^{1/2}$, $dm^{3/2}$ $mol^{-1/2}$ $s^{-1/2}$	$2fk_d$, $\times 10^5$, s^{-1}	C_m, $\times 10^5$	C_s, $\times 10^5$
DMBM	0.082	0.64	1.5	7.4
TMPM	0.27	1.23	2.6	1.1

[a] Solvent, benzene; temp, 60°C.

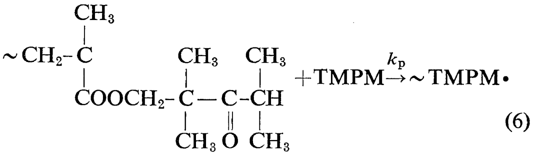
As shall be seen in Table II, the values of *e* of DMBM and TMPM are 0.69 and 0.32, respectively. Therefore, the electron density around the vinyl group of TMPM is larger than around that of DMBM. From this standpoint, the differences of $k_p/k_t^{1/2}$ and C_m in Table I can be explained as follows.

(i) For $k_p/k_t^{1/2}$. In the propagation, the following two cases are considered.



$$\sim CH_2-\underset{\underset{\underset{\underset{CH_3\;O}{|\quad\|}}{COOCH_2-C-C-CH_3}}{|\qquad\quad|}}{\overset{\overset{CH_3}{|}}{C\cdot}}\quad \overset{CH_3}{} \quad +DMBM \xrightarrow{k_p} \sim DMBM\cdot \qquad (5)$$

DMBM•



$$\sim CH_2-\underset{\underset{\underset{\underset{CH_3\;O\;CH_3}{|\quad\|\quad|}}{COOCH_2-C-C-CH}}{|\qquad\quad|\qquad|}}{\overset{\overset{CH_3}{|}}{C}}\quad \overset{CH_3\;\;CH_3}{} \quad +TMPM \xrightarrow{k_p} \sim TMPM\cdot \qquad (6)$$

TMPM•

The addition reaction of a free radical to the C=C bond proceeds through the following mechanism, according to Imoto and Takemoto.[2]

$$R\cdot + C{=}C \longrightarrow \underset{\text{CT-complex}}{[R^{+-}: C\text{–}C\cdot]} \longrightarrow R\text{–}C\text{–}C\cdot \qquad (7)$$

Therefore, when the density of free radical electrons in the propagating chain is larger, the formation of CT-complex becomes easier. From the *e*-values, it is assumed that the free radical density of TMPM• is larger than that of DMBM•. Accordingly, the rate of addition of R• to C=C in reaction 6 is easier than that in reaction 5; thus the k_p value of TMPM is larger than that of DMBM.

(ii) For C_s. C_s involves reactions 8 and 9.

$$DMBM\cdot + H\text{–}C_6H_5 \longrightarrow DMBM + \cdot C^6H_5 \qquad (8)$$

$$TMPM\cdot + H\text{–}C_6H_5 \longrightarrow TMPM + \cdot C_6H_5 \qquad (9)$$

The hydrogen abstraction reaction of a free radical R• with benzene proceeds through the following mechanism.[3]

$$R\cdot + H\text{–}C_6H_5 \longrightarrow \underset{\text{CT-complex}}{[R^-: H^+ \cdot C_6H_5]} \longrightarrow RH + \cdot C_6H_5 \qquad (10)$$

Accordingly, the radical R• with a larger unpaired electron density reacts with benzene with more difficulty than the radical R• with smaller unpaired electron density. Therefore, C_s in the case of TMPM is smaller than that in the case of DMBM.

(iii) For C_m. C_m is the reaction constant of the H• abstraction of the propagating chain from the monomer. TMPM has a tertiary hydrogen atom at the end of the molecule, as $-C(CH_3)_2H$, while DMBM does not have any tertiary hydrogen atom. Accordingly, C_m in TMPM is larger than that in DMBM.

(iv) For $2fk_d$. The term fk_d is affected very much by the "cage effect" of the surrounding molecules, which consist of benzene and monomer. The viscosity of a benzene solution of TMPM is found to be larger than that of DMBM. Accordingly, the theoretical comparison of the values of $2fk_d$ is not possible at the present time.

Copolymerization of DMBM

The copolymerization of TMPM with St was carried out in benzene at 60°C. The composition curve of the copolymer is shown in Figure 6.

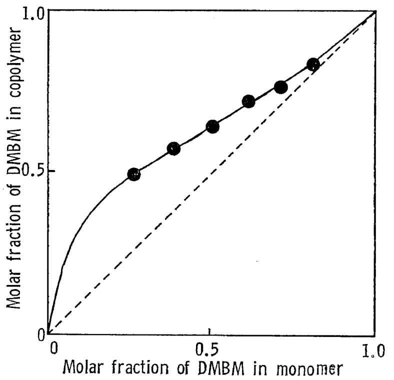


Figure 6. Copolymerization of DMBM with St: [Monomer]=2.21 mol dm^{-3}, [AIBN]=2.22×10^{-2} mol dm^{-3}; solvent, benzene; temp, 60°C.

The values of r_1 and r_2 obtained by the Fineman—Ross method and the values of Q and e for DMBM calculated from monomer reactivity ratios are listed in Table II and compared with those of TMPM.[1]

Table II. Parameters of copolymerization

M_1	M_2	r_1	r_2	Q_1[a]	e_1[a]
DMBM	St	0.97	0.11	2.73	0.69
TMPM[1]	St	1.78	0.14	2.55	0.32

[a] St: $Q_2=1.00$; $e_2=-0.80$.

The result that the r_1 value in the DMBM(M_1)—St(M_2) system is smaller than that in the TMPM(M_1)—St(M_2) system agrees with the smaller ratio $k_p/k_t^{1/2}$ of DMBM shown in Table I.

Prediction of the Values of Q and e for Vinyl Monomers from their λ_{max} and δ of ^{13}C NMR. We have previously deduced[1] eq 11, by which the Q-value could be calculated from the λ_{max} of the UV spectrum:

$$\log Q=5.175\times10^{-2}\,\lambda_{max}-10.880 \qquad (11)$$

Yuki, *et al.*,[4] confirmed that there was a linear relationship between $\delta_{c\beta}$ (the chemical shift of the β-carbon atom of the vinyl monomer in ^{13}C NMR) and the e-value. From that relationship, we introduced eq 12.

$$\delta_{c\beta}=-19.29e+78.57 \qquad (12)$$

Table III. Q, e-values

Monomer	λ^{a}_{max}, nm	Q from eq 11	$\delta_{c\beta}$[b]	e from eq 12
DMBM	219.7	3.09	67.21	0.59
TMPM	219.2	2.91	67.15	0.59

[a] Measured in EtOH. [b] Reference, CS_2.

The values of Q and e of DMBM and TMPM calculated from these equations were compared with the experimental values. They almost agreed, as seen in Table III.

The properties of poly-TMPM and poly-DMBM shall be described in another paper.

Acknowledgment. The present authors are very grateful to the Chisso Co. for supplying the isopropylmethyl ketone.

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