

A Kinetic Study of the Radical Polymerization of Polytetrahydrofuran Macromer

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ABSTRACT: The kinetics of the radical polymerization of *p*-vinylbenzyloxy- and *p*-vinylphenoxy-polytetrahydrofuran macromers were studied in dilute solutions at 60°C by a spectrophotometric method. In the case of an extremely low macromer concentration ($[C=C] < 1.6 \times 10^{-3} \text{ mol dm}^{-3}$), the rate of polymerization was independent of macromer concentration but proportional to the square root of initiator concentration. In addition, the degree of polymerization of recovered polymer was shown by GPC to be about unity in spite of the consumption of nearly all the vinyl groups of the macromer molecules. When the macromer concentration was above $1.6 \times 10^{-3} \text{ mol dm}^{-3}$, however, the kinetics of the radical polymerization were in accord with those of conventional vinyl monomers. These results are discussed in terms of the low concentration of vinyl groups of the macromer molecules.

KEY WORDS Kinetics / Radical Polymerization / Macromer / *p*-Vinylbenzyloxy-Polytetrahydrofuran / *p*-Vinylphenoxy-Polytetrahydrofuran / Spectrophotometric Method / Degree of Polymerization /

Recently, several papers¹⁻⁴ have been published on the syntheses of a variety of macromers and the radical polymerization and copolymerization of these macromers. However, no kinetic study of the polymerization of macromers has yet been reported. We have already succeeded in the syntheses of polytetrahydrofuran (PTHF) macromers, such as *p*-vinylbenzyloxy⁵ and *p*-vinylphenoxy⁶-PTHF (VBO- and VPO-PTHF) and their radical homopolymerization, and obtained high conversions; the degree of polymerization of the macromers was as high as 20 in benzene solutions.

Although we are studying the application of macromers to the preparation of graft and multi-branched polymers by the co- and homopolymerization of the macromers respectively, in this paper our interest is directed primarily to the kinetic study of the radical polymerization of macromers as macromolecular vinyl monomers. We believe that basic information on the kinetics of radical polymerization can be obtained through a comparison of macromer polymerization with that of conventional

vinyl monomers.

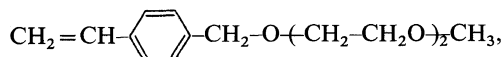
It was found that both VBO- and VPO-PTHF macromers facilitate the kinetic study of radical polymerization using a spectrophotometric method, since the PTHF moiety of the macromers scarcely has UV sensitivity whereas the styryl groups of the macromers have a very high UV absorbance in the range of 240—300 nm. In this study, we obtained kinetic data for the radical polymerization of both the macromers of VBO- and VPO-PTHF, intermittently measuring the rate of decrease in the vinyl groups by a UV spectrophotometer. The details of the kinetics of the radical polymerization of these macromers are reported.

EXPERIMENTAL

Materials

VBO- and VPO-PTHF macromers were prepared as reported previously.^{5,6} The number-average molecular weight of VBO-PTHF was 1.0×10^4 and those of VPO-PTHFs were 3.0×10^3 , 7.0×10^3 , and

1.0×10^4 , as determined by vapor pressure osmometry. These macromers were confirmed by UV spectrometry to have one vinyl group per molecule. *p*-Vinylbenzyl diglyme (VBDG):



as a model compound of VBO-PTHF was synthesized by the reaction of *p*-vinylbenzyl chloride with the sodium salt of diethylene glycol monomethyl ether according to the Williamson ether synthesis. Tetrahydrofuran (THF) used as a solvent for the radical polymerization was of UV spectro grade and distilled on a high vacuum line just before use, since THF exposed to air for a long period gives no reproducible results. α, α' -Azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Measurements

The initial rate of polymerization was determined as $R_p = -d[C=C]/dt$ by a spectrophotometric method using the polymerization cell shown in Figure 1. According to the concentration of vinyl groups in a polymerization system, quartz cells (Part C in Figure 1) of 0.15, 1.01, or 2.05 mm light paths were used and a monitored wavelength was chosen as 265 or 295 nm for VPO-PTHF and 252

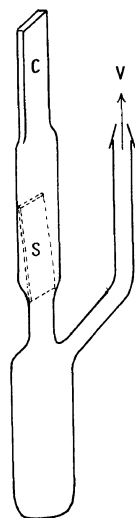


Figure 1. Polymerization cell: optical cell (quartz, 0.15–2.0 mm light path); S, spacer (1.85 mm-thick quartz plate); V, to a high vacuum line.

or 285 nm for VBO-PTHF and VBDG so that the initial absorbance obeyed Beer's law. For example (Exptl No. B-4), 47.0 mg of VBO-PTHF was placed in a polymerization cell (light path, 1 mm), and dissolved with 9.27 g of THF ($d^{60} = 0.842$) containing 4.83×10^{-3} wt% of AIBN. The cell was degassed on a high vacuum line ($< 10^{-2}$ Pa), sealed off, and then set in a water bath thermostated at 60.0°C. The decay of absorbance at $\lambda = 252$ nm was intermittently followed by a Hitachi Model 200-20 spectrophotometer. The absorbance–time curve was thus obtained and converted to the conversion–time curve as shown in Figure 2.

Gel permeation chromatograms (GPC) were recorded on a Toyo Soda HLC-802UR with two GMH columns (61 cm \times 2, Toyo Soda) for the analysis of the polymerization of the macromers and with G2000H₈ and G3000H₈ columns (61 + 61 cm, Toyo Soda) for the polymerization of VBDG. THF was used as the eluent and the flow rate was 1 cm³ min⁻¹.

RESULTS

Kinetics of the Radical Polymerization of PTHF Macromers

Radical polymerizations of VBO- and VPO-PTHF macromers were carried out at 60°C in THF using AIBN as the initiator. The polymerizations did not show any induction period in the time–conversion curves as evident from Figure 2. The

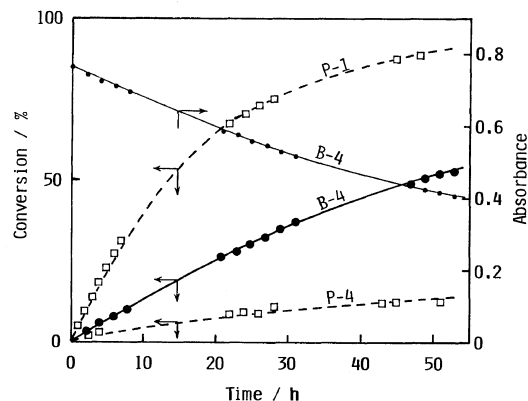


Figure 2. Time–absorbance and conversion (%) curves in Exptl No. B-4 and time–conversion in Exptl No. P-1 and P-4.

Table I. Kinetic data for the radical polymerization of VBO- and VPO-PTHF^a

Exptl No.	Macromer, $[M]_0 \times 10^4$ mol dm ⁻³	AIBN, $[I]_0 \times 10^4$ mol dm ⁻³	$R_p \times 10^7$ mol dm ⁻³ min ⁻¹
VBO-PTHF			
B-1	1.22	4.98	2.0
-2	4.27	4.98	2.0
-3	29.5	4.98	2.1
-4	4.27	2.48	1.0
-5	4.27	4.98	1.9
-6	4.27	24.8	3.8
VPO-PTHF ^b			
P-1	2.9	5.0	2.2
-2	9.8	5.0	2.4
-3	29.9	5.0	5.2
-4	98.0	5.0	13
-5	310	5.1	76
-6	5.1	2.4	0.9
-7	4.3	4.9	1.9
-8	4.5	25.0	3.6
-9	4.6	50.0	5.1

^a Polymn. temp, 60°C; solvent, THF.

^b $M_n, 7.0 \times 10^3$.

initial rate of polymerization (R_p) was determined from the slope of the curve in the initial stage. The results are summarized in Table I along with the polymerization conditions. In Figures 3 and 4, $\log R_p$ is plotted against $\log [I]_0$ and $\log [M]_0$, respectively. The former plots indicate that R_p is proportional to the square root of the initiator concentration. The latter plots show that the plotted lines bend at $[M]_0 = 1.6 \times 10^{-3}$ mol dm⁻³; *i.e.*, when the macromer concentration is above 1.6×10^{-3} mol dm⁻³, the polymerization is of the first order in the macromer concentration, whereas R_p is independent of macromer concentration at $[M]_0 < 1.6 \times 10^{-3}$ mol dm⁻³. Furthermore, Figure 4 shows that the polymerization rate and the novel kinetic behavior are hardly affected either by the molecular weight of the macromers or the structural difference between *p*-vinylbenzyloxy and *p*-vinylphenoxy groups. These results are summarized as follows:

$$R_p \propto [I]^{1/2}[M], \quad [M]_0 > 1.6 \times 10^{-3} \text{ mol dm}^{-3}$$

$$R_p \propto [I]^{1/2}[M]^0, \quad [M]_0 < 1.6 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{at } [I]_0 \approx 5 \times 10^{-4} \text{ mol dm}^{-3}.$$

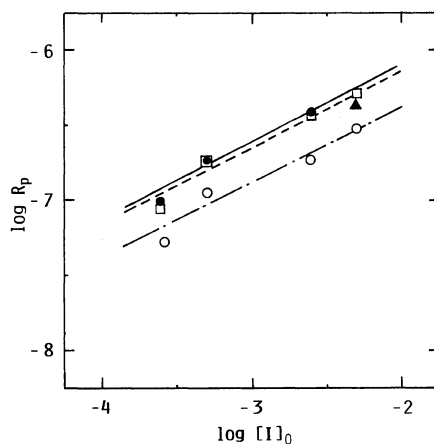


Figure 3. Plots of $\log R_p$ vs. $\log [I]_0$ in the radical polymerizations of VBO-PTHF (●), VPO-PTHF (○, $M_n, 1.0 \times 10^4$; □, $M_n, 7.0 \times 10^3$), and VBDG (▲) in THF ($[M]_0 \times 10^4, 3.8\text{--}8.6$ mol dm⁻³) at 60°C.

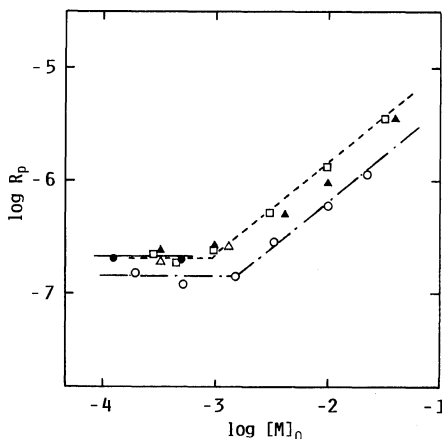


Figure 4. Plots of $\log R_p$ vs. $\log [M]_0$ in the radical polymerizations of VBO-PTHF (●), VPO-PTHF (○, $M_n, 1.0 \times 10^4$; □, $M_n, 7.0 \times 10^3$; △, $M_n, 3.0 \times 10^3$), and VBDG (▲) in THF at 60°C. The concentration of AIBN was *ca.* 5×10^{-4} mol dm⁻³.

The GPC curves of the polymers recovered in Exptl No. P-1 and P-5 are compared in Figure 5. When the concentration of the macromer was extremely low (Exptl No. P-1), the molecular weight of most of the macromer did not change and only a small part was polymerized to dimers at most although the consumption of the vinyl groups of the macromer was as high as 88% by UV analysis. In the case of a higher macromer concentration (Exptl

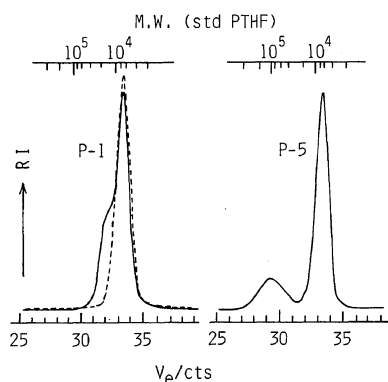


Figure 5. GPC curves of VPO-PTHF (---) and the polymers obtained at conversions of 88% and 31% in Exptl No. P-1 and -5, respectively.

Table II. Kinetic data for the radical polymerization of VBDG^a

Exptl No.	VBDG, $[M]_0 \times 10^4$ mol dm ⁻³	AIBN, $[I]_0 \times 10^4$ mol dm ⁻³	$R_p \times 10^7$ mol dm ⁻³ min ⁻¹
M-1	3.0	5.1	2.4
-2	9.9	5.0	2.6
-3	40	5.1	5.0
-4	100	5.0	9.3
-5	400	5.1	36
-6	8.6	4.9	1.9
-7	8.6	49	4.3

^a Polymn. temp, 60°C; solvent, THF.

No. P-5), however, the macromer was polymerized to a relatively high molecular weight poly-(macromer); for example, the degree of polymerization of poly(VPO-PTHF) in Exptl No. P-5 was estimated to be 10 from the peak of the GPC curve.

Kinetics of Radical Polymerization of VBDG

In order to confirm the novel kinetic behavior observed in the radical polymerization of the macromers, the radical polymerization of VBDG, considered to be a model compound, was carried out under the same conditions as the macromers. The results obtained showed that there is no significant difference between the radical polymerizabilities of the macromolecular monomer and the low molecular weight monomer. The initial rates of the polymerizations of VBDG at various initiator and VBDG concentrations are tabulated in Table II. The plots of $\log R_p$ versus $\log [I]_0$ and $\log [M]_0$ are shown in Figures 3 and 4, respectively.

Figure 6 shows the GPC curves of poly(VBDG)s formed in typical cases of polymerization. At an extremely low concentration of VBDG, *e.g.*, in Exptl No. M-1, the elution counts of the main peak of the GPC curve correspond to the molecular weight of an adduct of VBDG and an initiator fragment, and the amount of the dimer of VBDG was very little and that of the trimer was even much less. When the concentration of VBDG was 40 mmol dm⁻³ (Exptl No. M-5), VBDG was polymerized to poly(VBDG) whose molecular weight was as high as 3.0×10^3 (degree of polymerization ≈ 12) as estimated from the GPC curve.

These observations indicate that the kinetic be-

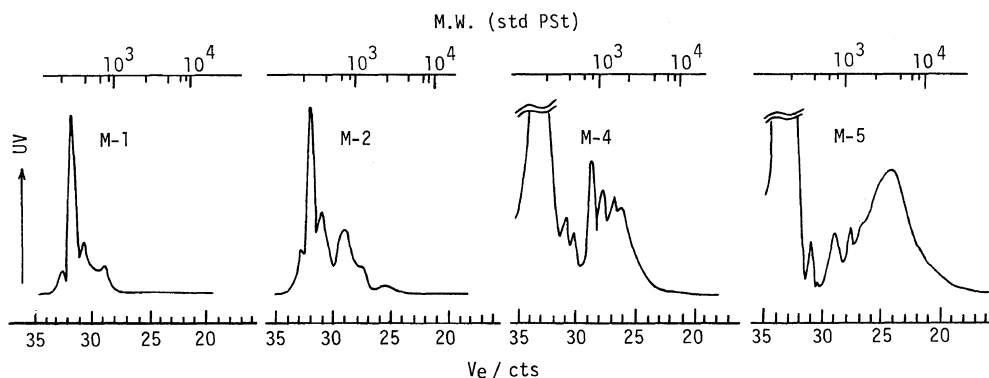


Figure 6. GPC traces of the oligomers obtained at conversions of 92%, 54%, 16%, and 13% in Exptl No. M-1, -2, -4, and -5, respectively.

havior of the radical polymerization of VBDG agrees with that of the macromers in dilute solutions.

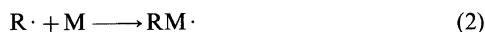
DISCUSSION

There are several reviews⁷ which described the polymer effect on radical polymerizations of vinyl monomers, which involves Trommsdorff's effect related to the non-stationary state of polymerization and the termination retarded by diffusion process. Therefore, it is reasonable to expect that the rate of polymerization of macromers would be slower than that of conventional vinyl monomers since the propagation of the macromer is a reaction between polymers as in the case of the termination. In this study, it may be concluded that there is no significant difference between the kinetics of the radical polymerization of macromers and that of conventional vinyl monomers and no dependence of the rate of polymerization and the degree of polymerization on the molecular weight of the growing polymer radicals. These facts certainly support Flory's assumption that the reactivity of polymer ends is not affected by the length of polymer molecules, even in a polymer-polymer reaction.

Dependence of R_p on the Concentrations of the Initiator and Macromer or VBDG

According to the kinetic results obtained in the radical polymerization of the macromers and VBDG, the following scheme is proposed:

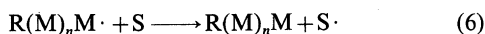
Initiation



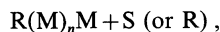
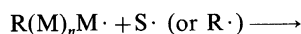
Propagation



Chain transfer



Termination



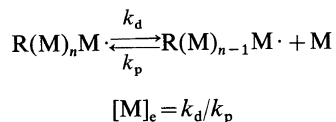
where I, R, M, and S denote initiator, fragment of initiator, macromer, and solvent, respectively. The same scheme as the macromer is also proposed for the radical polymerization of VBDG.

In polymerization at extremely low vinyl group concentrations ($[C=C] < 1.6 \times 10^{-3} \text{ mol dm}^{-3}$), probably propagation (eq 3) hardly takes place but the chain transfer to solvent (eq 5) should frequently occur, because the concentration of solvent is extremely high compared to that of the macromer. That is, the macromer must be consumed primarily by the reaction of eq 2 or 2'. The fact that R_p is independent of the macromer concentration suggests that the initiation (eq 2 and 2') is not a rate determining step of $-d[C=C]/dt$ and R_p is dependent on the concentration of radical species of $R \cdot$ and $S \cdot$ in a steady state. That the concentration of solvent is extremely high and the magnitudes of various chain transfer constants are of the order of 10^{-5} suggest that most of the radical species in the polymerization system are $S \cdot$ and thus the disappearance of radical species is exclusively due to the termination of eq 8. In consideration of the steady state of radical species, the following relations may hold, $2k_d f [I] = k_{iss} [S \cdot]^2 \propto [R \cdot]^2$. Thus, it can be understood that the rate of polymerization at an extremely low vinyl group concentration follows the square root rule, $R_p \propto [I]^{1/2}$.

When polymerization takes place at a relatively high concentration of vinyl groups ($[C=C] > 1.6 \times 10^{-3} \text{ mol dm}^{-3}$), the propagation according to eq 3 seemingly becomes so frequent that it can not be neglected. The rate expression thus agrees with the ordinary one; *i.e.*, $-d[C=C]/dt$ is proportional to $[I]^{1/2}$ and to $[M]$, $R_p \propto [I]^{1/2} [M]$.

As shown in Figure 4, all the plotted lines of $\log R_p$ versus $\log [M]_0$ for VBO-PTHF, VPO-PTHF, and VBDG bend at concentrations around $[M]_0 = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$. At present, there is no unequivocal interpretation as to why the critical turnings appear at low macromer concentrations such as

10^{-3} mol dm $^{-3}$, although it is suggested that either this critical concentration corresponds to an equilibrium concentration of the macromers ($[M]_e$),



or in this range of dilution, the chain transfer to solvent becomes much more predominant than the propagation of the macromers. Further study in regard to this is in progress.

Some recently published papers⁸ claim that the rate constants of radical polymerization depend on the molecular weight of polymer radicals. However, in this paper, it is conclusively indicated that the rate of polymerization as well as the rate constants and the degree of polymerization of the macromers do not depend on the molecular weight of the macromer. Furthermore, it is interesting that no significant difference in the kinetic results between the macromer and VBDG was observed.

As mentioned above, the GPC results of VBDG shown in Figure 6 also support the above conclusion for the kinetic results. In the polymerization of VBDG at a concentration as low as 10^{-3} mol dm $^{-3}$, the main product was an adduct of monomeric VBDG and an initiator fragment. This indicates that the polymerization of VBDG may be terminated mainly at the step of eq 2 or 2'. On the other hand, at a concentration of VBDG above 10^{-2} mol dm $^{-3}$, the GPC curve shows that poly(VBDG) is a major product and that the amount of monomeric VBDG is minor, implying that VBDG is converted primarily to the polymer according to the propagation of eq 3.

In conclusion, the novel kinetic feature proposed as a dual kinetic scheme at the critical concentration of the macromers stems merely from the low molar concentration of the macromers.

Degree of Polymerization of Poly(macromer)

It is well-known that the degree of polymerization in radical polymerization can be estimated from the following equation,⁹

$$\frac{1}{\bar{P}_n} = A \left(\frac{R_p}{[M]^2} \right) + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_P \frac{[P]}{[M]}$$

$$A = \frac{k_{tc} + 2k_{td}}{2k_p^2}, \quad R_p = k_p \left(\frac{2fk_d}{k_{tc} + k_{td}} \right)^{1/2} [I]^{1/2} [M]$$

By application of this equation to the case of the macromer, the degree of polymerization of poly(macromer) was calculated using the following constants⁹ for styrene: $k_{tc} = 3.6 \times 10^7$ dm 3 mol $^{-1}$ s $^{-1}$, $k_{td} = 0$, $k_p = 176$ dm 3 mol $^{-1}$ s $^{-1}$, $f = 0.8$, $k_d = 2.5 \times 10^{-5}$ s $^{-1}$, $C_M = 6 \times 10^{-5}$, $C_I = 0$, $C_S = 5.0 \times 10^{-5}$, and $C_P = 2.0 \times 10^{-5}$ (this value of C_P is for polyoxyethylene). The values calculated using the data of Exptl No. B-2 and P-5 were 0.6 and 36, and these values correspond to the observed values of 1 and 10 by GPC, respectively. Although the approximate estimation was performed using the rate constants for styrene, a fairly good agreement between the calculated and observed values was demonstrated.

This fact again confirms that the low degree of polymerization of poly(macromer) is not ascribed to polymer effects on the reactivity of the macromer, but to the low molar concentration of the macromer.

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