Molecular Weight in Polymerization of Methyl Methacrylate Initiated with Cyclohexanone

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MOLECULAR WEIGHT IN POLYMERIZATION OF METHYL METHACRYLATE INITIATED WITH CYCLOHEXANONE

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ABSTRACT

Molecular weight investigations of the poly(MMA) obtained in the polymerization initiated with cyclohexanone were carried out. The chain-transfer constants to the monomer, solvent, and initiator, using a new formal approach for chain-transfer constants calculations based on the Mayo relation, have been evaluated: $C_M = 1.1 \times 10^{-3}$, $C_I = 2.2 \times 10^{-4}$, $C_S = 1.8 \times 10^{-4}$. The comparatively high C_M value is interpreted in terms of the increased susceptibility of the MMA molecules toward the chain-transfer reaction due to the interactions between the monomer and initiator molecules. The influence of the temperature on the $\overline{DP}_n$ of poly(MMA) is correlated with activation energy of initiation E_i of MMA polymerization initiated with cyclohexanone.

INTRODUCTION

It has been reported that some active organic compounds containing active hydrogen atoms can initiated the radical polymerization and copolymerization of polar vinyl monomers [1–4]. It is known that when the C-atom is attached to the electron-withdrawing atom or group, such as an oxygen atom or a carbonyl group,

any hydrogen attached to the carbon becomes weakly acidic. Organic compounds with this type of hydrogen atoms undergo many ionic reactions, e.g., the metalation reaction. Simultaneously, the same hydrogen atoms are the most reactive ones in various radical reactions. It was shown for cyclohexanone that the hydrogen atom abstracted in a radical reaction comes from one of the two carbon atoms in the α-position [5, 6]. The mechanism of the initiation reaction involving transfer of the hydrogen radical abstracted from the active compound to the monomer was originally proposed by Ouchi et al. [2] for the polymerization of methyl methacrylate (MMA) initiated with aldehydes (RCHO). A similar type of interaction between methyl methacrylate and cyclohexanone molecules resulting in the formation of radicals in a polymerization system has been proposed [3]. As a result, the polymerization reaction of MMA can start and propagate as shown in Scheme 1.

Ouchi et al. [2] reported that with an increase in the concentration of (RCHO), a decrease in the number-average degree of polymerization, $\overline{DP}_n$, of poly(MMA) was observed. In their opinion it can explain some chain transfer reactions. However, no further investigations in have been performed and no attempts to determine particular transfer constants have been made.

More detailed investigations of the molecular weights of polymers obtained in similar polymerization reactions seem to be applicable to more precisely establish their mechanism.

The present paper deals with molecular weight investigations of the poly-(MMA) obtained in polymerization reactions initiated with cyclohexanone under different conditions. Also, a new formal approach for chain-transfer constant calculations based on the Mayo relation is proposed.

EXPERIMENTAL

The materials and the polymerization procedure in dioxane were described previously [3].

The number-average molecular weight of poly(MMA) was measured in toluene at 301 ± 0.1 K using a Knauer Membrane Osmometer. The osmotic pressure was measured with an accuracy of 0.5%. The membrane used was made of regenerated cellulose acetate.
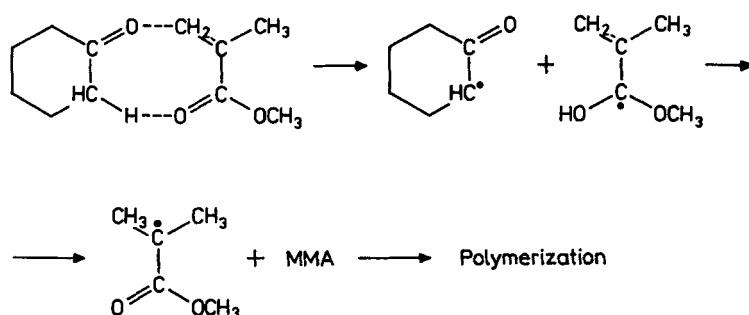
SCHEME 1.

THEORETICAL DEVELOPMENT

Determination of Transfer Constants

In an earlier article it was shown that the overall rate of a reaction initiated with cyclohexanone (R_p) is proportional to the concentration of MMA and to the square root of the concentration of the initiator [7]. This means that the polymerization kinetics of the investigated reaction is described by the general polymerization equation developed for the ideal radical-initiated vinyl polymerization. This fact induced us to use the fundamental Mayo relationship [8] in its adapted form for the determination of chain-transfer constants in the present system. In spite of the possible uncertainties, a correlation can be drawn between the magnitudes of chain-transfer constants and the monomer, solvent, and initiator behavior in the polymerization system.

For the ideal solvent vinyl polymerization, $R_p = k[M][I]^{0.5}$. The relationship between the number-average degree of polymerization $\overline{DP}_n$ and the chain-transfer constants in defined by the well-known Mayo equation:

$$\frac{1}{\overline{DP}_n} = C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + \frac{\delta^2}{[M]^2} R_p \tag{1}$$

Using volumes instead of concentrations, Eq. (1) can be transformed into

$$\frac{1}{\overline{DP}_n} = C_M + C_S S \frac{V_S}{V_M} + C_I I \frac{V_I}{V_M} + P \frac{V_I^{0.5}}{V_M} \tag{2}$$

where

$$S = \frac{d_S W_M}{W_S d_M}$$

$$I = \frac{d_I W_M}{W_I d_M}$$

and, assuming that for ideal polymerization $R_p = k[M][I]^{0.5}$,

$$P = \frac{\delta^2 k W_M d_I^{0.5} V^{0.5}}{d_M W_I^{0.5}}$$

d, W, and V are density, molecular weight, and total volume of the polymerization mixture, respectively. Indexes M, I, and S correspond to monomer, initiator, and solvent, respectively.

Case I

The polymerization reaction is carried out with a constant total volume of the reaction mixture and constant monomer volume (concentration), V and V_M, respectively.

Making the substitution $V_S = V - V_I - V_M$ and transforming Eq. (2), we obtain

$$\frac{1}{\overline{DP}_n} = A_1 + A_2 V_I + A_3 V_I^{0.5} \tag{3}$$

where A_1, A_2, and A_3 are constants and have the following meanings:

$$A_1 = C_M + C_S S \frac{V - V_M}{V_M}$$

$$A_2 = \frac{C_I I - C_S S}{V_M}$$

$$A_3 = \frac{P}{V_M}$$

Case II

The polymerization reaction is carried out with a constant total volume of the reaction mixture and a constant initiator volume, V and V_I, respectively. Making the substitution $V_S = V - V_I - V_M$ and transforming Eq. (2), we obtain

$$\frac{1}{\overline{DP}_n} = B_1 + B_2 \frac{1}{V_M} \tag{4}$$

where B_1 and B_2 are constant and have the following meanings:

$$B_1 = C_M - C_S S$$
$$B_2 = C_S S(V - V_I) + C_I V_I I + P V_I^{0.5}$$

Using the least-squares fitting method, parameters A_1, A_2, A_3 and B_1, B_2 in Eqs. (3) and (4), respectively, can be estimated.

From A_1 and B_1 the transfer constants C_M and C_S can be calculate and, subsequently, the transfer constant C_I.

RESULTS AND DISCUSSION

Applicability of the Mayo Equation

To use the Mayo equation to determine transfer constants, some necessary conditions during polymerization must be fulfilled: low thermal rate of polymerization, low conversion of the monomer, no polymer precipitation during the reaction, etc. One of the most important conditions is the constancy of the velocity coefficients of the component reactions, such as k and f, irrespective of the concentrations of the solvent, monomer, and initiator [9]. The most common method of proving the applicability of the Mayo equation to the polymerization system is to show that the k value from the overall kinetic equation $R_p = k[M][I]^{0.5}$ remains constant with variations in the concentrations of the reaction components, e.g., [S]/[M].

The $R_p/[M][I]^{0.5}$ ratio vs concentration of the reaction components is shown in Fig. 1. The calculated standard deviation of $k = 1.33 \pm 0.12 \times 10^{-5}$ $L^{1/2} \cdot$ $mol^{-1/2} \cdot s^{-1/2}$ is small. Thus, the $R_p/[M][I]^{0.5}$ ratio can be regarded as almost constant in the investigated (quite wide) concentration range of the particular reaction components. For low concentrations of the solvent and initiator, however, a comparatively higher deviation in the calculated k values can be observed.

$$\frac{[I]}{[M]}$$
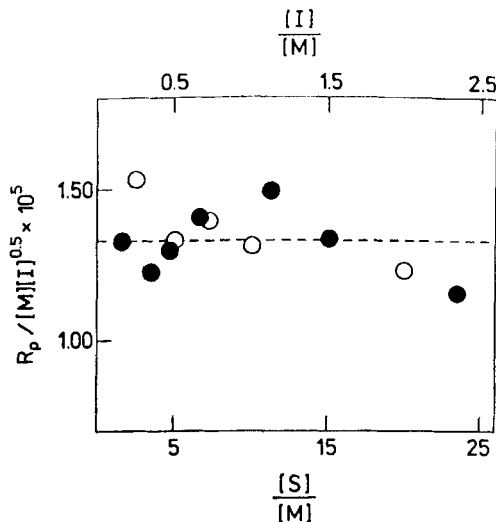
FIG. 1.   Polymerization of MMA (M) at 75°C in dioxane (S) initiated with cyclohexanone (I). The $R_p/[M][I]^{0.5}$ ratio vs $[S]/[M]$ and $[I]/[M]$. (○) $[M]$ = constant = 1.57 mol/L. (●) $[I]$ = constant = 1.61 mol/L. (---) Calculated average value of k = 1.33 ± 0.12 × 10^{-5} $L^{1/2} \cdot mol^{-1/2} \cdot s^{-1/2}$.

Determination of Transfer Constants

The polymer samples used for the osmometric measurements had monomer conversions under 12 wt%. Since the molecular weight of the polymer obtained did not change significantly after an hour of reaction time (Fig. 2), probably reaching steady-state conditions, samples with 1.5–2.0 hours of reaction time were taken for

FIG. 2.   Variation of $\overline{DP}_n$ of poly(MMA) with the time of MMA polymerization at 75°C in dioxane. [MMA] = 3.15 mol/L, [Chn] = 1.61 mol/L.

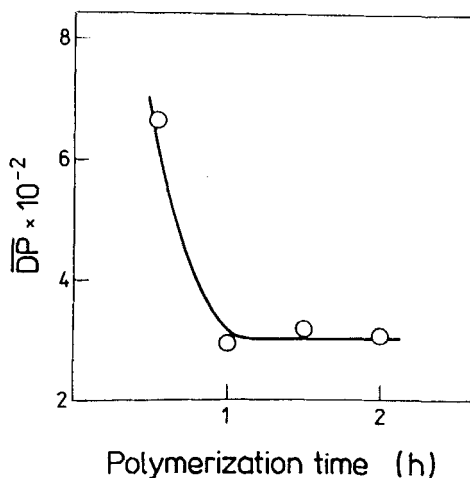further investigation. It will be shown later that the $\overline{DP}_n$ of the polymer obtained decreases rapidly with increasing temperature. It is clear that in the time period before the polymerization temperature has reached 75°C, the molecular weight of the polymer formed is comparatively higher and raises the $\overline{DP}_n$ obtained in the initial stages of polymerization.

The poly(MMA) samples for the determination of transfer constants were obtained in two series of polymerization reactions. During the first series of reactions, corresponding to Case I above, the polymerization was performed while keeping the monomer concentration constant. During the second series of reactions, corresponding to Case II above, the initiator concentration was kept constant. In both series the total volume of the reaction mixture, V, was kept constant at 24 mL.

The number-average degree of polymerization, $\overline{DP}_n$, calculated from the osmometric measurements for Case I and Case II, are presented in Table 1 (Fig. 3) and Table 2 (Fig. 4), respectively.

As seen from Figs. 3 and 4 a monotonous decrease and increase in $1/\overline{DP}_n$ with an increase in the concentrations of MMA and cyclohexanone, respectively, can be observed. There is one exception, however; as seen from the Fig. 3, a very high concentration of MMA in the polymerization system (8 mL MMA of the total volume of polymerization system $V = 24$ mL) results in a comparatively low $\overline{DP}_n$. Decreasing of the $\overline{DP}_n$ of poly(MMA) obtained in the polymerization system with that high concentration of MMA is probably due to the simultaneous thermal polymerization of MMA at a temperature of 348 K producing many comparatively short poly(MMA) chains since the thermal polymerization of MMA probably always accompanies the polymerization of the monomer at the elevated temperature [10–12]. It seems that the effect of the thermal polymerization becomes more predominant in polymerization with a molar excess of MMA when compared to Chn present in the reaction mixture. It is worth noting that in the polymerization of MMA initiated with active methylene compounds, including cyclohexane, a similar effect of the high monomer concentration on monomer conversion has been observed. Thus, data on the influence of the [Initiator]/[MMA] ratio in a wide range (from ca. 0.4 to 2.0) on the polymerization of MMA carried out by keeping the

TABLE 1. Influence of Monomer Concentration (MMA) on the $\overline{DP}_n$ of Poly(MMA)[a]

No.	Volume of Chn, mL	Concentration of Chn, mol/L	$\overline{DP}_n \times 10^{-2}$
1	1	0.39	1.32
2	1.5	0.59	1.68
3	2	0.79	2.88
4	3	1.18	3.12
5	4	1.57	3.90
6	5	1.96	4.11
7	8	3.15	2.56

[a]Solvent: dioxane, [Chn] = constant = 1.61 mol/L, V = 24 mL, T = 75°C.
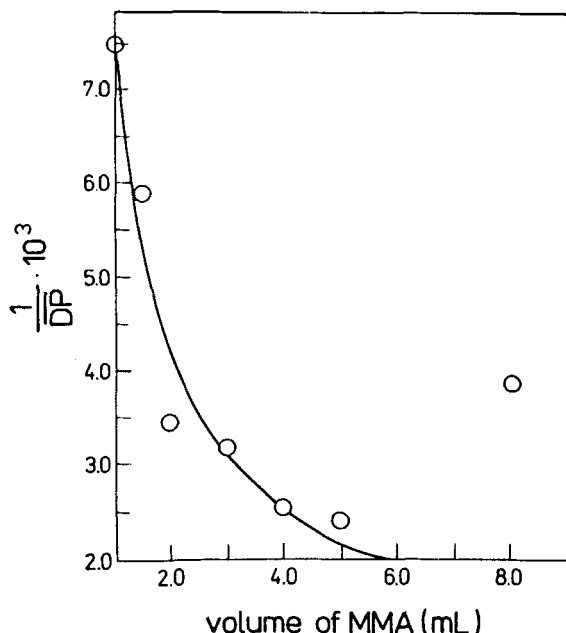
FIG. 3. Influence of the monomer concentration [MMA] on the $1/\overline{DP}_n$ of poly-(MMA). Solvent: dioxane, [MMA] = constant = 1.18 mol/L, total volume of polymerization system V = 24 mL, T = 75°C. The curve was calculated by the least squares fitting method.

monomer concentration constant at 1.57 mol·L^{-1} and varying the concentration of the methylene compounds (cyclic ketones, acetyl acetone, diethyl malonate, and ethyl acetoacetate) showed that for an [Initiator]/[MMA] ratio of 0.8–1.2 the maximal conversions of MMA were obtained [13]. Therefore, the $\overline{DP}_n$ of poly(MMA) obtained with the maximal volume of MMA (3.15 mol·L^{-1}), and therefore proba-

TABLE 2.   Influence of Initiator Concentration [Chn] on the $\overline{DP}_n$ of Poly(MMA)[a]

No.	Volume of Chn, mL	Concentration of Chn, mol/L	$\overline{DP}_n \times 10^{-2}$
1	1	0.40	4.49
2	2	0.81	4.00
3	3	1.21	3.79
4	4	1.61	3.12
5	6	2.42	2.27
6	8	3.23	1.95

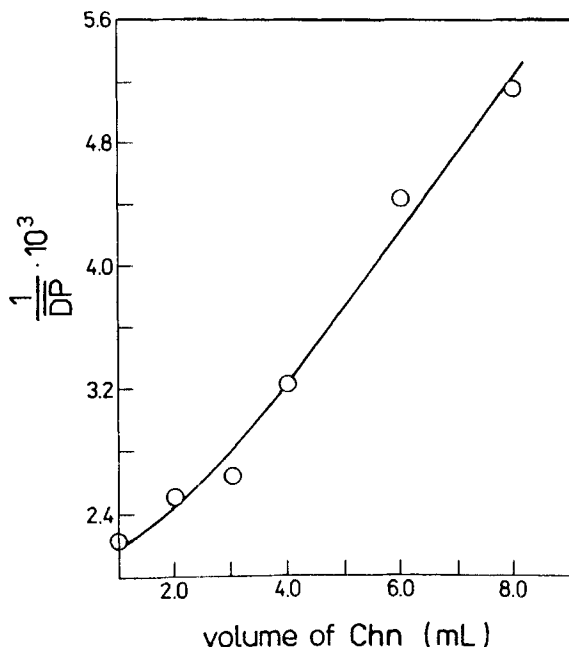[a]Solvent: dioxane, [MMA] = constant = 1.18 mol/L, V = 24 mL, T = 75°C.

FIG. 4. Influence of the initiator concentration (Chn) on the $1/\overline{DP}_n$ of poly(MMA). Solvent: dioxane, [Chn] = constant = 1.61 mol/L, total volume of polymerization system $V = 24$ mL, $T = 75°C$. The curve was calculated by the least squares fitting method.

bly containing a comparatively substantial part of the thermal polymerized monomer, has not been used for further chain-transfer constants calculations.

The results of the least-squares method calculations for the parameters A_1, A_2, A_3 in Eq. (3) and B_1, B_2 in Eq. (4) are presented in Table 3.

Now, the monomer, initiator, and solvent chain-transfer constants, C_M, C_I, and C_S, respectively, have been calculated: $C_M = 1.1 \times 10^{-3}$, $C_I = 2.2 \times 10^{-4}$, $C_S = 1.8 \times 10^{-4}$. As seen from these results, the highest chain-transfer constant value has been obtained for methyl methacrylate. For comparison, the literature

TABLE 3. The Results of the Least-Squares Fitting Method Calculations of Parameters A_1, A_2, A_3 and B_1, B_2 in Eqs. (3) and (4), Respectively

Calculated value	Case I			Case II	
Adjustable parameter	A_1	A_2	A_3	B_1	B_2
	2.691	0.7618	−1.254	0.8825	6.751
Standard deviation of the parameter, σ	$\sigma(A_1)$	$\sigma(A_2)$	$\sigma(A_3)$	$\sigma(B_1)$	$\sigma(B_2)$
	0.7465	0.2127	0.8270	0.4171	0.7397
Correlation coefficient for the pair of parameters, q	$q(A_1,A_2)$	$q(A_1,A_3)$	$q(A_2,A_3)$	$q(B_1,B_2)$	
	0.9482	−0.9818	−0.9897	−0.8719	

data of various monomer, initiator, and solvent chain-transfer constants can be found in Ref. 14.

The chain-transfer constant obtained for dioxane, $C_S = 1.8 \times 10^{-4}$, does not vary much from the data published in the literature. It is in good agreement with the data for polymerization of MMA in the solvent at 40°C using the charge-transfer complex as photoinitiator, $C_S = 5 \times 10^{-4}$ [15] or 8.3×10^{-4} [16], and conventional free radical initiator at 80°C, $C_S = 0.222 \times 10^{-4}$ [17].

As mentioned before, the chain-transfer constant for cyclohexanone was calculated to be $C_I = 2.2 \times 10^{-4}$. No comparative data have been found for the chain-transfer constant to cyclohexanone in the polymerization of MMA. For the radical polymerization of methyl acrylate however, the chain-transfer constant to cyclohexanone at 80°C was reported to be 5.5×10^{-4} [18]. Thus, the value is very similar to that measured by us for MMA polymerization.

The computed C_M value for the MMA monomer, $C_M = 1.1 \times 10^{-3}$, is about two orders higher than that reported in the literature for the conventional initiated radical solution polymerization of MMA. Considering the data obtained however, it should be pointed out that there are comparatively few representative data about the influence of the solvent on the calculated C_M values for the MMA monomer. Kinetic studies done by Gopalan et al. provided necessary data [19]. Thus, the chain-transfer constants of poly(MMA) radical with monomer during free radical initiated polymerization in bulk, ethyl methyl ketone, ethyl acetate, and benzene at 75°C (at the temperature used in our experiments) were calculated by Gopalan et al. to be 0.33×10^{-4}, 0.60×10^{-4}, 0.27×10^{-4}, and 0.70×10^{-4}, respectively. These results show that the influence of the solvent on the calculated C_M is not very significant, and that it does not depend only on the polarity of the solvent used. The C_M value increases for an aliphatic ketone and benzene and decreases for ethyl acetate when compared to bulk polymerization. However, all the values are of the same order.

Taking into account the formal definition of C_M $(= k_{tr,M}/k_p)$, obtained by measuring the relative rates of reaction of monomer with the propagating radical for the transfer and propagation reaction, the comparatively high chain-transfer constant in our system, $C_M = 1.1 \times 10^{-3}$, can be regarded as result of the increased susceptibility of the MMA molecules toward the chain-transfer reaction. Since methyl methacrylate does not undergo degradative chain transfer [20], no evidence of retardation accompanying monomer transfer is observed, so no changes in k_p should be noticed. Thus, the increased susceptibility of the MMA molecules toward the chain-transfer reaction is due to the increased $k_{tr,M}$. As shown in the schema above, interactions between the monomer and initiator molecules increase the electron-withdrawing effect of the carbonyl group of MMA toward hydrogen atoms from the α-methyl, enhancing their susceptibility to transfer reaction. The resonance structure of the radical formed as a result of chain transfer to the α-methyl of the methyl methacrylate molecule (Scheme 2) [21] becomes, when complexed with cyclohexanone, more stabilized.

Effect of Temperature

The influence of the temperature on the $\overline{DP}_n$ of poly(MMA) is shown in Fig. 5. As expected, the degree of polymerization of the product polymer decreases rapidly with increasing temperature. In a homogeneous polymerization, since the
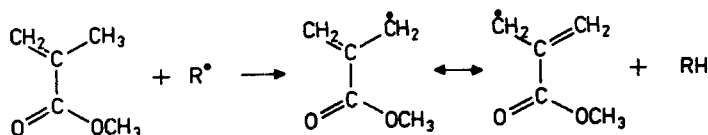
SCHEME 2.

activation energy for initiation of conventional initiated polymerization is much greater than either that for propagation or termination, the degree of polymerization obtained is expected to decrease with increasing polymerization temperature. It was calculated previously [7] that the overall activation energy E_a and the activation energy of initiation E_i for the polymerization of MMA in dioxane initiated with cyclohexanone in a temperature range of 65-95°C are 134 kJ·mol^{-1} and 232-237 kJ·mol^{-1}, respectively. The E_i value of 232-237 kJ·mol^{-1} is much higher than the values obtained with conventional radical initiators like azo compounds or peroxides. Their average activation energy of decomposition is about 130 kJ·mol^{-1} [22]. Thus, the high E_i value for the polymerization of MMA initiated with cyclohexanone explains the strong dependence of the $\overline{DP}_n$ of poly(MMA) on the polymerization temperature.

CONCLUSIONS

From the results obtained it can be concluded that of all particular transfer processes the most significant influence on the $\overline{DP}_n$ of the polymer produced in the polymerization of MMA initiated with cyclohexanone is not the expected chain-
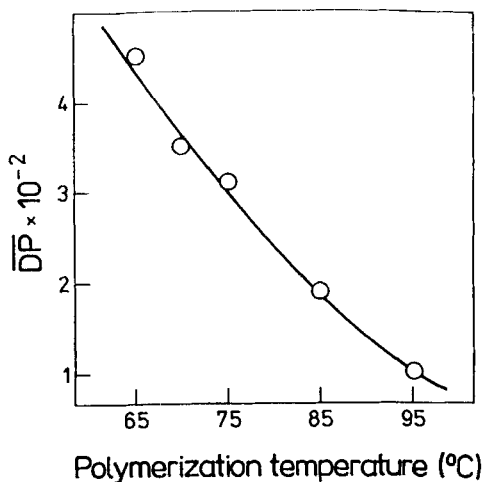
FIG. 5. Variation of $\overline{DP}_n$ of poly(MMA) with the temperature of MMA polymerization in dioxane. [MMA] = 1.18 mol/L, [Chn] = 1.61 mol/L, polymerization time t = 2 hours.

transfer to cyclohexanone but to monomer. On the other hand, despite of the questionable C_I and C_S values obtained, the magnitude of the C_M led us to accept this value with caution. Thus, further investigations on both the application of the least-squares fitting method for the calculation of chain-transfer constants and the interactions between methyl methacrylate and cyclohexanone molecules are necessary.

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