Radical Copolymerization Between Methyl Methacrylate and *N*-cyclohexylmaleimide with Thiol as an Inifer

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ABSTRACT: *N*-dodecanethiol (RSH) was found efficient to initiate the radical copolymerization of methyl methacrylate (MMA) with *N*-cyclohexylmaleimide (NCMI) at 40–60°C. The initial copolymerization rate, R_p, increases respectively with increasing [RSH] and the mol fraction of NCMI in the comonomer feed, f_{NCMI}. The molecular weight of the copolymer decreases with increasing [RSH]. The initiator transfer constant of RSH was determined to be $C_I = 0.21$. The apparent activation energy of the overall copolymerization was measured to be 46.9 kJ/mol. The monomer reactivity ratios were determined to be $r_{\text{NCMI}} = 0.32$ and $r_{\text{MMA}} = 1.35$. The glass transition temperature of the copolymer increases obviously with increasing f_{NCMI}, which indicates that adding NCMI may improve the heat resistance of plexiglass. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1417–1423, 1999

Key words: methyl methacrylate; *N*-cyclohexylmaleimide; thiol; copolymerization; inifer

INTRODUCTION

N-substituted maleimides have become interesting monomers that can be either radically copolymerized with other vinyl monomers[1,2] or homopolymerized[3–6] by radical and anionic initiators despite their 1,2-disubstituted ethylene structure. Many works on their radical polymerization and copolymerization have been performed so far because of the superiority of their polymer in thermal stability.[7]

Thiols are widely used as chain transfer agents in free radical polymerization to regulate the molecular weight of resulting polymers. However, it was reported that thiol alone can initiate not only the copolymerization of charge transfer complex (CTC) comonomers such as styrene/acrylonitrile[8] and styrene/*N*-phenylmaleimide,[9] etc., but also the copolymerization of non-CTC comonomers such as methyl methacrylate (MMA)/acrylonitrile.[10] In the polymerization systems mentioned, thiol plays a role as inifer which acts as both initiator and chain transfer agent. In this work, the kinetics of the copolymerization of MMA/*N*-cyclohexylmaleimide (NCMI) initiated by thiol was studied, and the initiator transfer constant of *N*-dodecanethiol (RSH) was measured. In addition, the experimental data show that the resulting copolymer has good transparency and thermal stability.

EXPERIMENTAL

Materials

Raw materials were purified by standard procedures. MMA (Shanghai Chemical Reagents Com-

pany) was distilled under reduced pressure immediately before use. NCMI (Zhuozhou Haihui Chemicals Co. Ltd., Hebei Province, P.R. China), a commercial product, recrystallized twice from dry acetone, was dried in vacuum before use. RSH (Aldrich), A.R. grade, was used without further purification.

Polymerization

Copolymerization was performed in dilatometers as mentioned[8] previously. The monomer conversion was controlled to be less than 10% by mol. The initial polymerization rate (in $mol \cdot m^{-3} \cdot s^{-1}$) is given in eq. (1).

$$R_p = \Delta V / [\bar{M}_0 \cdot V_0 (1/d_0 - 1/d_p)] \tag{1}$$

where $\bar{M}_0$ is the average-molecular weight of the monomer units in copolymer; $1/d_p$ is the specific volume of copolymer; $1/d_0$ is the specific volume of the monomer mixture, of which the composition is the same as that of the respective copolymer [where d_0 and d_p were rectified (see Appendix)]; V (in $m^3 \cdot s^{-1}$) is the contraction of the reactant volume; V_0 is the initial reactant volume.

Analysis and Characterization

The density was measured by a pycnometer, the copolymer composition was calculated from nitrogen elemental analysis (Heraus Rapid, CHN–0), and molecular weight was determined by means of gel permeation chromatography (GPC) equipped with a Waters 410 Differential Refractometer, and calibrated with poly(methyl methacrylate) (PMMA) linear standards. The glass transition temperature (T_g) of copolymer was measured by differential scanning calorimetry (DSC) (PE Pyris-1 Series) in a flowing nitrogen atmosphere (the heating rate was 10°C/min).

RESULTS AND DISCUSSION

Kinetic Study on Copolymerization of MMA with NCMI

The kinetic study was implemented at 50°C using methyl ethyl ketone (MEK) as the solvent. In the absence of RSH, no polymerization was observed in the reaction system of MMA and NCMI. When a trace amount of RSH was added, the copolymerization occurred within 0.5 h at the same reaction
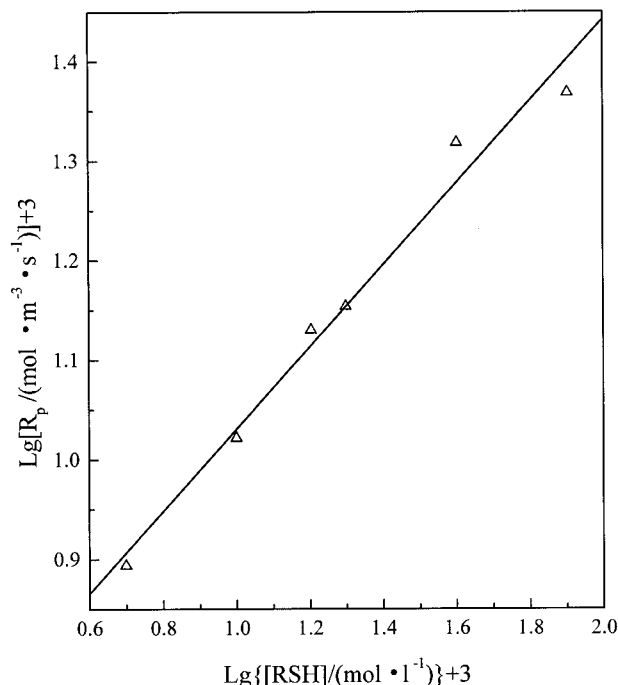
Figure 1 Relationship between initial copolymerization rate, R_p, and thiol concentration, [RSH]; [MMA] = [NCMI] = 1.0M, solvent: MEK, temperature: 50°C.

temperature. Hence, RSH does initiate the copolymerization of MMA with NCMI.

The influence of the concentration of RSH on the initial polymerization rate, R_p, was examined over a wide range. When [RSH] is $5.0 \times 10^{-3}M$ $- 8.0 \times 10^{-2}M$, R_p is proportional to $[RSH]^{0.41}$, as shown in Figure 1, which indicates that thiol plays a double role, i.e., the initiator and the chain transfer agent. Because R_p is proportional to the initiator concentration to the power of 0.5 in a bimolecular termination process and the concentration of a chain transfer agent has little influence on R_p, the chain transfer from propagating radicals to thiol results in an exponent of [RSH] less than 0.5. In addition, phenol can inhibit the copolymerization, therefore the free radical feature of the reaction is confirmed.

The effects of [RSH] on the molecular weight of the resultant copolymer were studied (Table I). $\bar{M}_w$ and $\bar{M}_n$ of the copolymer decrease with increasing [RSH], and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) became narrower with increasing [RSH]. Figure 2 shows that the slope of the plot of lg $\bar{M}_n$ vs. Lg[RSH] is -0.656, between -0.5 and -1.0, which also indicates that RSH serves as both an initiator and a chain transfer agent, i.e., RSH serves as inifer in this copolymerization system.

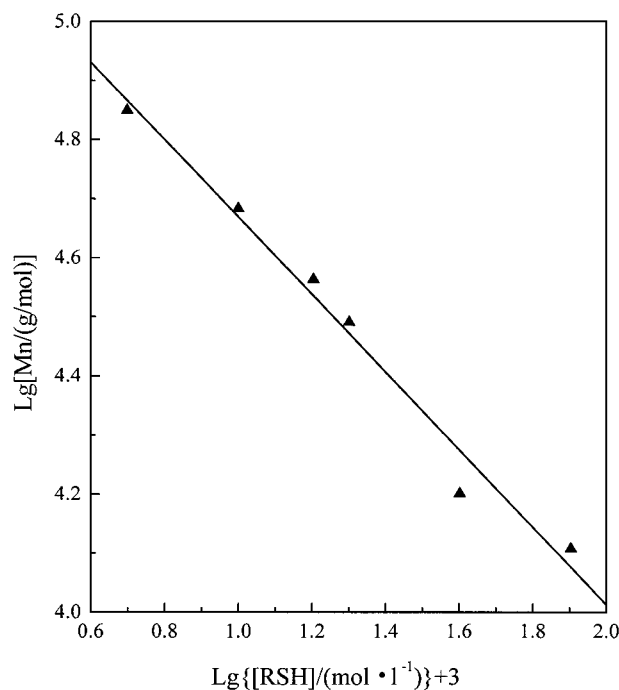**Table I   Relationship Between Molecular Weight and [RSH]; [MMA] = [NCMI] = 1.0M, Solvent: MEK, Temp: 50°C**

[RSH], 10^{-3} mol/l	5	10	16	20	40	80
$\bar{M}_n$, 10^4 g/mol	7.07	4.82	3.65	3.09	1.59	1.07
$\bar{M}_w$, 10^4 g/mol	11.94	7.51	5.44	4.58	2.23	1.40
$\bar{M}_w/\bar{M}_n$	1.69	1.56	1.49	1.48	1.40	1.30

To determine the initiator transfer constant (C_I) of RSH, we rearrange eq. (3-121) of Reference[11] and divide it by R_p to yield

$$\left[\frac{1}{X_n}\right]\frac{1}{R_p} = \frac{k_t}{k_p^2[M_0]^2} + C_I\frac{[I]}{R_p[M_0]} \qquad (2)$$

where X_n is the copolymerization degree calculated according to eq. (3) (F_{NCMI} is the mol fraction of NCMI in the copolymer composition. NCMI and MMA molecular weights are 179 and 100).

$$X_n = \bar{M}_n/[179F_{NCMI} + 100(1\text{-}F_{NCMI})] \qquad (3)$$

A plot of the left side of eq. (2) vs. $[I]/R_p[M_0]$ yields a straight line, whose slope is C_I. From Figure 3 we get the value of $C_I = 0.21$ for RSH initiated copolymerization of MMA and NCMI in MEK solution at 50°C, which is very close to the value of $C_s = 0.22$ in the 2,2′-azobisisobutyronitrile(AIBN) initiated copolymerization of MMA and NCMI in benzene solution with RSH as a chain transfer agent in the reference.[12]

The influence of reaction temperature on R_p as well as the molecular weight of copolymer was studied in the range of 40–60°C. The plot of ln R_p vs. 1/T is given in Figure 4. From the slope of the

Figure 2 Relationship between $\bar{M}_n$ and [RSH]; [MMA] = [NCMI] = 1.0M, solvent: MEK, temperature: 50°C.
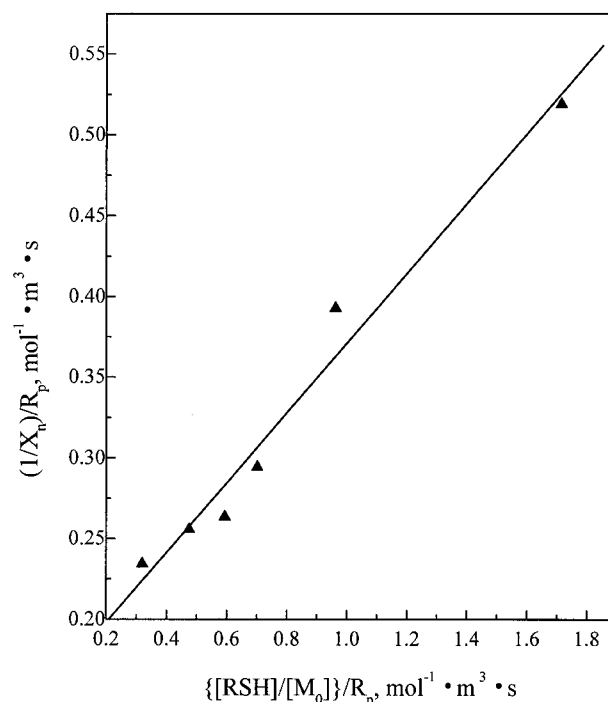
Figure 3 Determination of initiator chain transfer constant in the RSH initiated copolymerization of MMA and NCMI in MEK solution at 50°C, $[M_0]$ = [MMA] + [NCMI], [MMA] = [NCMI] = 1.0M.
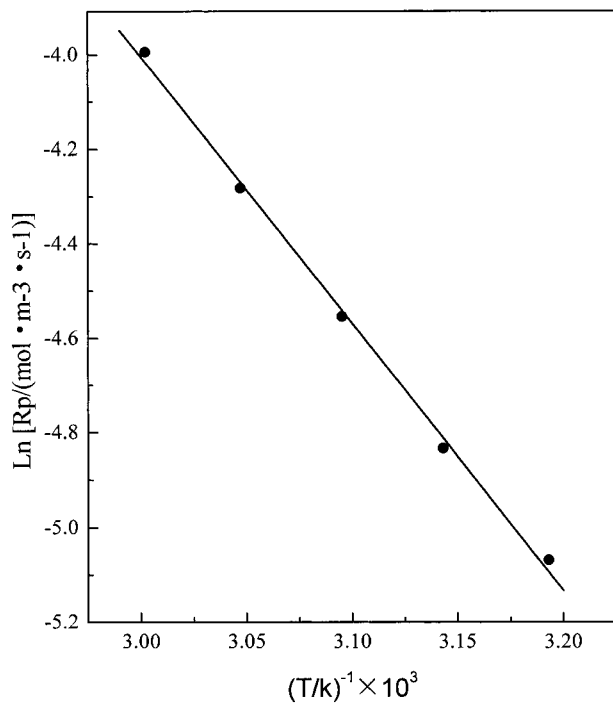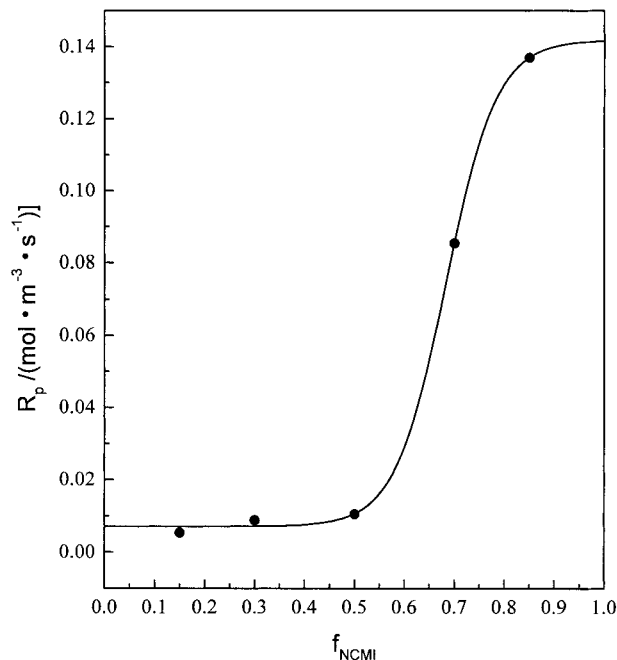
Figure 4 Arrhenius plot for the variation of R_p with temperature; [MMA] = [NCMI] = 1.0M, [RSH] = 0.01M; solvent: MEK.

Figure 5 Relationship between R_p and mol fraction of NCMI in comonomer feed; [MMA] + [NCMI] = 2.0M, [RSH] = 0.010M, solvent: MEK, temperature: 50°C.

straight line the apparent activation energy of the overall copolymerization, Eapp, is calculated to be 46.9 KJ/mol, which is much lower than that of most polymerization initiated by thermal initiator decomposition (80–90 KJ/mol).[11] Table 2 shows that, $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ slightly increase with the rising of the temperature. This is probably due to the RSH served as both an initiator and a chain transfer agent.

The effects of monomer composition on R_p and molecular weight have also been investigated. R_p increases with the increase of the mol fraction of NCMI in the MMA/NCMI feed (f_{NCMI}) (Fig. 5). $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ also increase with increasing f_{NCMI}, but X_n does not change very much, as shown in Table 3.

Copolymer Composition

The monomer reactivity ratios were evaluated to be $r_{NCMI} = 0.32$ and $r_{MMA} = 1.35$ in terms of the Y-B-R method[13] using the copolymerization data in Table III. In the meantime, the Kelon-Tüdős approach[14] was also used to deal with the experimental data of Table III (see Fig. 6:

$$\eta = \frac{f_{NCMI} \times (F_{NCMI} - F_{MMA})/(f_{NCMI} \times F_{NCMI})}{\alpha + (f_{NCMI}/f_{MMA})^2/(F_{NCMI}/F_{MMA})},$$

$$\xi = \frac{(f_{NCMI}/f_{MMA})^2/(F_{NCMI}/F_{MMA})}{\alpha + (f_{NCMI}/f_{MMA})^2/(F_{NCMI}/F_{MMA})},$$

$$\alpha = 1.87).$$

Table II   Relationship Between Molecular Weight and Temperature; [MMA] = [NCMI] = 1.0M, [RSH] = 0.010M, Solvent: MEK

| Temperature, K	313	318	323	328	333
$\bar{M}_n$, 10^4 g/mol	4.73	4.84	4.82	4.98	5.19
$\bar{M}_w$, 10^4 g/mol	7.25	7.18	7.51	8.19	10.97
$\bar{M}_w/\bar{M}_n$	1.54	1.48	1.56	1.65	2.12

Table III   Copolymerization Data for NCMI and MMA at 50°C; [MMA] + [NCMI] = 2.0M, [RSH] = 0.010M, Solvent: MEK

f_{NCMI}	0.15	0.30	0.50	0.70	0.85
N content in copolymer, %	1.44	2.41	4.06	5.16	6.28
F_{NCMI}	0.112	0.199	0.376	0.520	0.694
$\bar{M}_n$, 10^4 g/mol	4.64	5.01	4.82	5.67	5.60
X_n	426	433	372	402	362
$\bar{M}_w$, 10^4 g/mol	6.60	7.36	7.51	9.13	10.36
$\bar{M}_w/\bar{M}_n$	1.42	1.47	1.56	1.61	1.85
T_g, K	402.3	414.5	445.6	452.0	473.7

Plotting η vs. ξ in Figure 6, we obtain a straight line, which extrapolated to $\eta = 0$ and $\xi = 1$ gives $-r_{MMA}/\alpha = -0.728$ and $r_{NCMI} = 0.32$ (both as intercepts), i.e., $r_{MMA} = 1.36$. So we can conclude that the copolymerization follows Mayo-Lewis kinetics. These results are also in agreement with those reported by Matsumoto and coworkers[7] ($r_{NCMI} = 0.24$ and $r_{MMA} = 1.35$ in the copolymerization system with benzene as solvent and AIBN as initiator). The fact of $r_{NCMI} < 1$ and $r_{MMA} > 1$ means that radicals preferentially add to MMA instead of NCMI, i.e., the activity of MMA is greater than the activity of NCMI in this copolymerization system. $r_{NCMI} \times r_{NCMI} < 1$ means that the copolymerization of MMA and NCMI has a weak tendency toward alternative one. Figure 7 shows the diagram calculated from the Mayo-Lewis equation. Experimental results are illustrated in the same Figure. It is seen that the experimental points and the theoretical cure are in good agreement. It seems unnecessary to introduce a penultimate effect for explaining the experimental results, and the presence of RSH does not affect the way in which the chain radicals propagate.
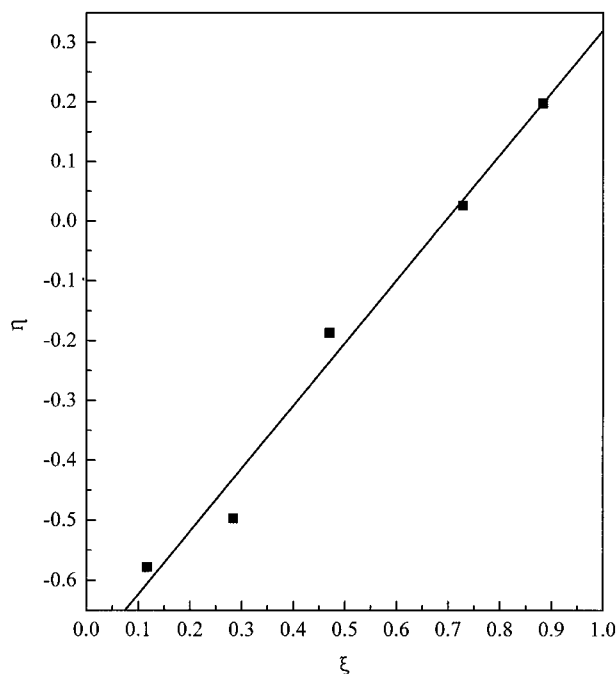
Figure 6 Copolymerization data for NCMI and MMA at 50°C, plotted according to the Kelon-Tüdős method[14]; [MMA] + [NCMI] = 2.0M, [RSH] = 0.010M, solvent: MEK.
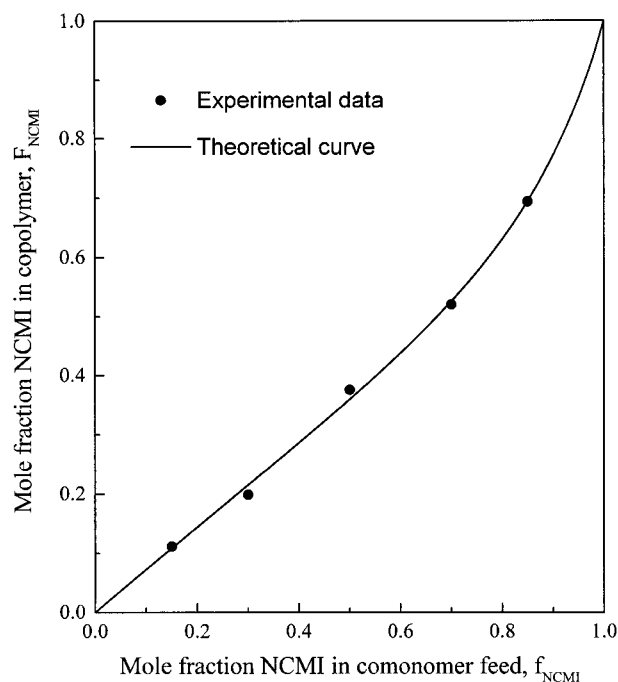
Figure 7 Copolymer composition diagram; [MMA] + [NCMI] = 2.0M, [RSH] = 0.010M, solvent: MEK, temperature: 50°C.

As we know, the copolymerization of CTC comonomer usually leads to an alternative copolymer.[8,9] However, the diagram of the copolymer composition in Figure 7 ($F_{NCMI} < f_{NCMI}$) indicates that the resultant copolymer is not a strong alternative one. We may come to the conclusion that the copolymerization of MMA with NCMI initiated by RSH does not involve in CTC.

Table III also shows that T_g of copolymer increases obviously with increasing the content of feed NCMI in the copolymerization system. The T_g of PMMA is 105°C.[11] So adding NCMI can improve greatly the thermal resistance of plexiglass.

APPENDIX

In general, the volume of a solution is not equal to the total volume of the unmixed (pure) components at constant temperature and pressure, we have to introduce the partial molar volume to evaluate $1/d_0$ and $1/d_p$ in the eq. (1).

Let V be the volume of a dilute solution of density d_0' with MEK as solvent, MMA and NCMI as solutes, and suppose the partial molar volume $\bar{V}_v$ of the solvent MEK approximately equals its molar volume $\bar{V}_v^*$. We have

$$
\begin{aligned}
V &= n_0\bar{V}_0 + n_v\bar{V}_v \\
&= n_0\bar{V}_0 + n_vV_v^* \\
&= V\{[MMA] + [NCMI]\}(\bar{M}_0/d_0) + V_v^*\{d_0' \times V \\
&\quad - V \times [NCMI] \times 179 - V \\
&\quad \times [MMA] \times 100\}/M_v \\
&= \frac{V}{d_0}\{[NCMI] \times 179 + [MMA] \times 100\} \\
&\quad + \frac{V}{d_v}\{d_0' - [NCMI] \times 179 - [MMA] \times 100\}
\end{aligned}
$$

(A1)

where n_0 is the total mol number of NCMI and MMA; n_v is the mol number of solvent MEK; $\bar{V}_0$ is the average partial molar volume of NCMI and MMA, dm³/mol; $\bar{M}_0$ is the average molecular weight of NCMI and MMA; M_v is the molecular weight of solvent MEK; $1/d_0$ is the specific volume of the monomer mixture, dm³/g; $1/d_v$ is the specific volume of solvent MEK, dm³/g; [NCMI] and

[MMA] are the concentrations of NCMI and MMA in moles per liter (dm³); 179 and 100 are the molecular weights of NCMI and MMA. Therefore

$$
\frac{1}{d_0} = \frac{1}{d_v} - \frac{d_0' - d_v}{d_v\{[NCMI] \times 179 + [MMA] \times 100\}}
$$

(A2)

Similarly, let V be the volume of a dilute solution of density d_p' with MEK as solvent and MMA, NCMI, and a little copolymer as solutes, and suppose that the partial molar volume $\bar{V}_v$ of the solvent MEK is approximately equal to its molar volume $\bar{V}_v^*$ and the effect of a little copolymer on $\bar{V}_v$ is negligible. We have

$$
\begin{aligned}
V &= n_0\bar{V}_0 + n_v\bar{V}_v + n_p\bar{V}_p \\
&= \frac{V}{d_0}\{[NCMI] \times 179 + [MMA] \times 100\} \\
&\quad \times (1 - \alpha) + \frac{V}{d_v}\{d_p' - [NCMI] \times 179 \\
&\quad - [MMA] \times 100\} + \frac{V}{d_p}\{[NCMI] \\
&\quad \times 179 + [MMA] \times 100\}\alpha
\end{aligned}
$$

(A3)

where n_p is the mol number of the copolymer; $\bar{V}_p$ is the partial molar volume of the copolymer, dm³/mol; α is the weight ratio of the copolymer to the solutes (NCMI, MMA, and copolymer); $1/d_p$ is the specific volume of the copolymer, dm³/g. Hence

$$
\frac{1}{d_p} = \left\{\frac{1}{d_v} - \frac{1 - \alpha}{d_0} - \frac{d_p' - d_v}{d_v([NCMI] \times 179 + [MMA] \times 100)}\right\}/\alpha
$$

(A4)

So, by the aid of eqs. (A2) and (A4) we can calculate $1/d_0$ and $1/d_p$ respectively in a given concentration solution using MEK as solvent and MMA, NCMI, and a little copolymer as solutes.

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