

## SOLVENT EFFECT IN THE COPOLYMERIZATION OF METHYL METHACRYLATE WITH OLIGOGLYCOL DIMETHACRYLATE

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**Abstract**—Methyl methacrylate was radically copolymerized with oligoglycol dimethacrylate using dioxane or *n*-butyl acetate as good and poor solvents, respectively. The delay between actual gel point and the theoretical one was much larger in a good solvent. The primary chain length, closely related to gelation, was relatively shortened for the polymer obtained in a poor solvent. The occurrence of intramolecular cyclization, leading to the formation of loop structures, was reduced in a poor solvent. The relationships between intrinsic viscosity or root-mean square radius of gyration and weight-average molecular weight were found and they are discussed in terms of the solvent effect on intramolecular cyclization and crosslinking.

### INTRODUCTION

In our previous article [1], the gelation behaviour in the copolymerization of methyl methacrylate (MMA) with oligoglycol dimethacrylates  $[\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{COC}(\text{CH}_3)=\text{CH}_2]$  (OGMA) ( $n = 1, 2, 3, 4, 9, 14$  and  $23$ ) has been examined; gelation was delayed by changing the number of oxyethylene units from  $n = 1$  to  $n = 2$ , but, interestingly, beyond the value of two, gelation was accelerated with increase in the number of oxyethylene units. This effect was ascribed to the increased primary chain length estimated by the extrapolation of the conversion dependence of weight-average molecular weight  $\bar{M}_w$  to zero conversion. In the preceding article [2], the enhanced primary chain length caused by increasing the number of oxyethylene units was discussed in detail; it was attributed to the suppression of the intermolecular termination between growing polymer radicals having a loop structure formed through intramolecular cyclization.

This article is concerned with a solvent effect in the copolymerization of MMA with PEGMA-400 ( $n = 9$ ) as a typical OGMA because the chain-mobility of the resulting prepolymer would be reflected in the occurrence of intramolecular cyclization leading to the formation of loop structures; the delay of the observed gel point from the theoretical [3] was much larger in a good solvent than in a poor solvent and the primary chain length was reduced in a poor solvent.

### EXPERIMENTAL

Monomers, 2,2'-azobisisobutyronitrile (AIBN) as an initiator, 1,4-dioxane (DOx) as a good solvent, and *n*-butyl acetate (BuAc) as a poor solvent were prepared as described [1].

Polymerization was carried out in ampoules. The polymer produced was precipitated by pouring the reaction mixture into a large amount of methanol. The gel fraction of the polymer samples obtained at a conversion beyond the gel

point was separated by extracting the sol fraction with tetrahydrofuran (THF).

$\bar{M}_w$  was measured by light scattering (LS) measurements carried out in THF at  $30 \pm 0.1^\circ$  in a Union Giken LS-601 automatic laser scattering photogoniometer over the angular range between  $30$ – $150^\circ$ , using unpolarized light of wavelength  $632.8$  nm. The intrinsic viscosity  $[\eta]$  of the polymer was measured in THF solution at  $30^\circ$  in a Ubbelohde viscometer.

GPC-LALLS measurements were carried out with a Waters Associates ALC/GPC 244 apparatus at room temperature under the following conditions: solvent, THF;  $\mu$ -styragel column combination,  $10^2$ ,  $500$ ,  $10^3$ ,  $10^4$  and  $10^5$  Å (Waters designation); polymer concentration,  $0.1\%$  (w/v); and flow rate,  $1$  ml/min. The dual detector system consisted of a LALLS and a differential refractometer in sequence in the flow direction. The LALLS was a LS-8000 manufactured by TOSOH Corporation, where the laser beam of wavelength  $632.8$  nm was focused on a  $30$   $\mu$ l flow cell. The scattering angle was always  $5^\circ$ .

### RESULTS AND DISCUSSION

#### *Solvent effect on gelation*

The choice of DOx and BuAc as good and poor solvents, respectively, was made on the basis of LS and  $[\eta]$  data in various solvents.

Figure 1 shows the time vs conversion curves for the solution copolymerization of MMA with PEGMA-400,  $1$  mol% of which was employed as a crosslinker for MMA, in DOx or BuAc (volume ratio total monomer/DOx or BuAc =  $1:4$ ) using  $0.04$  mol/l of AIBN at  $50^\circ$ . The percentage of gel polymer obtained by sol-gel separation is also plotted against time in Fig. 1. The gel point was estimated to be  $24.6$  and  $28.8\%$  in DOx and BuAc, respectively. The gel point was a little higher in a poor solvent than in a good solvent.

It should be noted that the primary chain length, which is closely related to gelation [3], was quite different for polymers obtained using DOx and BuAc as shown in Fig. 2; the primary chain length is estimated by extrapolation of each curve to zero

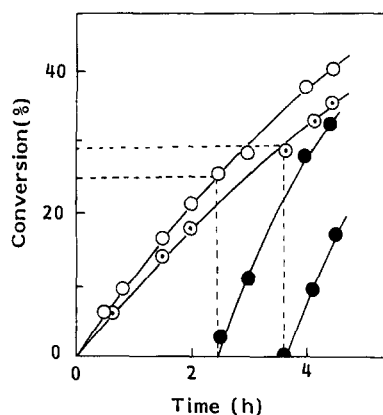


Fig. 1. Time-conversion curves for the solution copolymerizations in DOx (○) and BuAc (●): ○, ●, total polymer; ●, gel polymer.

conversion. Thus the theoretical gel points were calculated according to Stockmayer's equation [3]; the results are summarized in Table 1. The difference between actual and theoretical gel points was increased in a good solvent. This is in line with the solvent effect on the gelation of the polymerization of diallyl phthalate and -terephthalate and the copolymerization of methyl methacrylate with ethylene dimethacrylate [4] contrary to Walling's result [5].

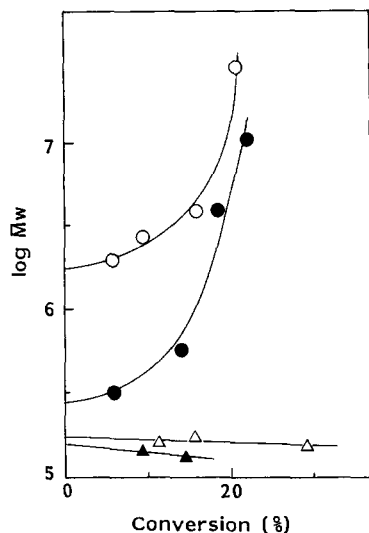


Fig. 2. Dependence of  $\bar{M}_w$  on conversion in the solution copolymerizations in DOx (○) and BuAc (●), along with MMA homopolymerizations in DOx (△) and BuAc (▲).

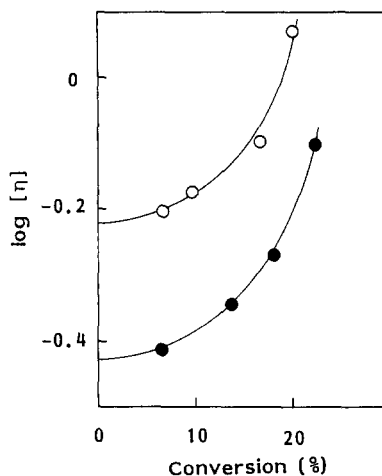


Fig. 3. Dependence of  $[\eta]$  on conversion in the solution copolymerizations in DOx (○) and BuAc (●).

#### *Solvent effect on intramolecular cyclization and intramolecular crosslinking*

As seen in Fig. 2, the molecular weights of the polymers obtained in BuAc were less than those in DOx, although they are still higher than that of MMA homopolymer. It should be noted that the difference was only small for MMA homopolymers. Thus the great reduction of the molecular weight in BuAc suggests reduced intramolecular cyclization leading to the formation of loop structures and the subsequent suppression of the intermolecular termination between growing polymer radicals as compared with the case in DOx [2]; this effect may have arisen from a tighter coiling and less mobility of both MMA-main chain and polyoxyethylene-side chains because of a poor solvent power of BuAc.

The formation of loop structures should cause decrease in the hydrodynamic volume of the resulting polymer. In this connection, the intrinsic viscosities of the polymers were measured and plotted against conversion in Fig. 3. The intrinsic viscosity  $[\eta]_0$  of the primary chain was then estimated by extrapolating the curve to zero conversion and compared to that of a presumed linear chain, which was calculated by using the molecular weight of the primary chain [2], as summarized in Table 2. The value of  $[\eta]_0/[\eta]_L$  in BuAc was quite large compared to that in DOx as expected; this result is in line with the reduced occurrence of intramolecular cyclization in BuAc as a poor solvent.

This kind of intramolecular cyclization should

Table 1. Gelation in MMA-PEGMA-400 copolymerization<sup>a</sup>

Solvent	Gel point (%)	$\bar{P}_{w,0} \times 10^{-3}$	Theoretical gel point <sup>b</sup> (%)	Actual G.P.
				Theoretical G.P.
DOx	24.6	17.4 (1.85) <sup>c</sup>	0.29	84.8
BuAc	28.8	2.77 (1.75) <sup>c</sup>	1.82	15.8

<sup>a</sup>Total monomer/solvent = 1:4 (v/v); [PEGMA-400] = 1 mol%; [AIBN] = 0.04 mol/l; 50°.

<sup>b</sup> $\alpha_c = 1/\rho(\bar{P}_{w,0} - 1)$ .

<sup>c</sup>MMA homopolymerization.

Table 2. Deviation of primary chain from linearity

Solvent	$\bar{M}_{w,0} \times 10^{-5}$	$[\eta]_0$ (dl/g)	$[\eta]_0/[\eta]_L^*$
DOx	18.1	0.604	0.25
BuAc	2.88	0.380	0.64

\* $[\eta]_L = 4.24 \times 10^{-5} \bar{M}_{w,0}^{0.76}$ .

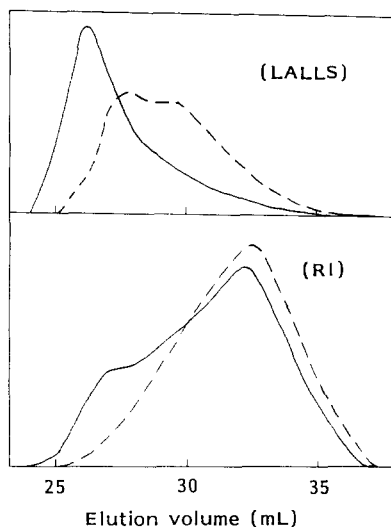


Fig. 4. GPC-LALLS curves of the copolymers obtained in DOx (—) and BuAc (---).

occur more significantly in a more diluted solution and in the presence of a higher added amount of crosslinker. Thus, polymerization was carried out under the following polymerization conditions: PEGMA-400 1.5 mol%, in DOx or BuAc (volume ratio monomer/DOx or BuAc = 1:7),  $[AIBN] = 0.04$  mol/l, at  $50^\circ$ . Gel points were obtained as 36.6 and 73.0% in DOx and BuAc, respectively. The ratios of actual to theoretical gel points were calculated to be 113 and 38, again indicating the greatly delayed gelation in DOx as a good solvent. Figure 4 shows GPC-LALLS curves of the polymers obtained

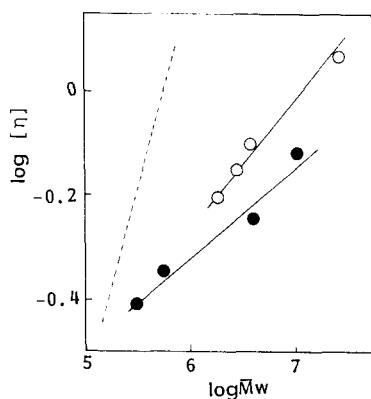


Fig. 5. Relationships between  $[\eta]$  and  $\bar{M}_w$  in the solution copolymerizations in DOx (○) and BuAc (●). Dashed line corresponds to MMA homopolymerization.

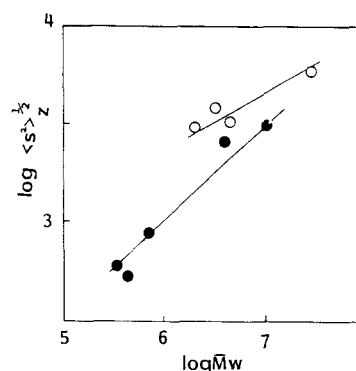


Fig. 6. Double logarithmic plots of  $\langle S^2 \rangle_z^{1/2}$  vs  $\bar{M}_w$  in the solution copolymerizations in DOx (○) and BuAc (●).

at around 7% conversion, the weight-average molecular weights of which were determined as  $1.67 \times 10^6$  (DOx) and  $2.86 \times 10^5$  (BuAc) by LS. The intensity of LS of the high molecular weight portions at a low elution volume was clearly observed to be high for the polymer obtained in DOx, indicating the enhanced occurrence of intramolecular cyclization.

Figure 5 shows the relationship between  $\bar{M}_w$  and  $[\eta]$  based on the data in Figs 2 and 3, along with that of poly (MMA); both plots of the MMA-PEGMA-400 copolymers obtained in DOx and BuAc were placed below that of poly(MMA) and the slopes were quite low, although the value of  $[\eta]$  of the copolymer obtained in BuAc was much lower. These results are interpreted by considering the occurrence of intramolecular cyclization and intramolecular crosslinking, the latter becoming more significant with the progress of polymerization, i.e. with an increase in  $\bar{M}_w$ . That is, the small deviation from a linear poly-(MMA) for the polymer obtained at an early stage of polymerization in BuAc solution is a consequence of reduced occurrence of intramolecular cyclization; the large deviation at a later stage of polymerization comes from more pronounced intramolecular crosslinking through enhanced interpenetration of the polymer chains in a poor solvent.

Figure 6 shows double logarithmic plots of root-mean square radius of gyration ( $\langle S^2 \rangle_z^{1/2}$ ) vs  $\bar{M}_w$ ; the upper location for the polymer obtained in DOx corresponds reasonably to the intrinsic viscosity data shown in Fig. 5. Furthermore, this may be relevant to the enhanced occurrence of intramolecular cyclization leading to the broad molecular weight distribution in DOx because the value of  $\langle S^2 \rangle_z^{1/2}$  is  $z$ -averaged.

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