MECHANISM OF THREE-DIMENSIONAL POLYMERIZATION OF GLYCOL METHACRYLATES. IV.*

THE SYSTEM TRIGLYCOL MONOMETHACRYLATE–GLYCOL DIMETHACRYLATES–WATER

J.Kopeček and D.Lím

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

Earlier papers of this series[1−3] have been dealing with the laws of the three-dimensional polymerization of glycol monomethacrylate and more hydrophilic diglycol monomethacrylate with a small amount of dimethacrylates. Although the possibilities of application of glycol monomethacrylate are greater, owing to a rather insignificant dependence of its properties on the polymerization conditions, than those of diglycol monomethacrylate, the latter is more suited for the investigation of both the kinetics of polymerization and structure over the whole range of conversions for experimental reasons.

The object of the present work has been an investigation of the polymerization of the system triglycol monomethacrylate–glycol dimethacrylates–water which proceeds within the whole range of water concentrations in the homogeneous phase, in contrast with the lower members of this series of monoesters, where separation of phases occurs at the limit concentration of water.

EXPERIMENTAL

Triglycol monomethacrylate was prepared by re-esterification of methyl methacrylate. The diester was removed from the water-diluted reaction mixture by extracting with the mixture light petroleum-ether (3 : 1). The monoester obtained by distillation, b.p. 121°C/0·4 Torr, n_D^{20} 1·4581, contained a low amount of diester (< 0·05%), which can be determined from the equilibrium degree of swelling of the polymerization product up to 100% conversion. Glycol dimethacrylate and triglycol dimethacrylate were prepared by a procedure described earlier[1].

The polymerization technique in dilatometers (using azo-2,2′-bis(methyl isobutyrate) as initiator and cetane as the measuring liquid) at 60°, as well as the measurement of the equilibrium degree of swelling have been described in an earlier work[1].

RESULTS AND DISCUSSION

It has been established for the copolymerization of triglycol monomethacrylate (M) with triglycol dimethacrylate as the crosslinking agent (in an amount lower by an order of 10^2 with respect to M) in an aqueous medium that the reaction order with respect to the monomer in the region of low conversions (with no gel-effect) is 0·7 (Fig. 1). In the hydrophilic systems under study, the reaction order with respect to the monomer increases only very little in the following series of monomers: glycol, diglycol- (cf.[1−3]), and triglycol monomethacrylate (0·5; 0·6; 0·7, respectively); this seems especially surprising in the case of the copolymerization of triglycol monomethacrylate, which opposite to the lower monoesters occurs without phase separation within the whole range of water concentrations. The reaction rates with respect to the monomer established by the

---

authors can formally be explained in terms of the dependence of the propagation and termination rate constants on the properties of the medium[1,2]. These constants can be defined as follows:

$$k'_p = k_p[M]^a ; \qquad (1)$$

k_p is the propagation constant in the actual kinetic sense (dimension being $1 \text{ mol}^{-1} \text{ s}^{-1}$), k'_p is
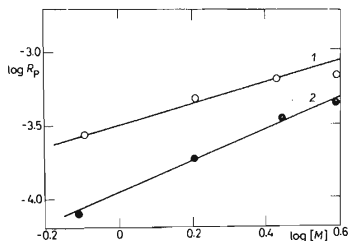
FIG. 1

Dependence of the Rate of Copolymerization, R_p, in the System Triglycol Monomethacrylate–Triglycol Dimethacrylate–Solvent on the Monomer Concentration

1 Aqueous solution, concentration of azo-2,2'-bis(methyl isobutyrate) as the initiator $c_i = 5\cdot3 \cdot 10^{-3}$ mol/l, *2* ethanol solution, $c_i = 5\cdot8 \cdot 10^{-3}$ mol/l.
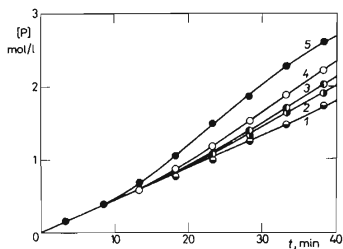
FIG. 2

Course of the Copolymerization of Triglycol Monomethacrylate (M) with Triglycol Dimethacrylate (M_c)

[M] = $3\cdot39$ mol/l; [H_2O] = $16\cdot34$ mol/l; $c_i = 5\cdot06 \cdot 10^{-3}$ mol/l. [M_c] . 10^2 mol/l: *1* 0; *2* 0·44; *3* 1·03; *4* 2·07; *5* 4·08.

the effective propagation constant, whose physical meaning has been slightly changed, since it involves the properties of the surrounding medium; and a is a constant;

$$k'_1 = k_1[M]^b ; \tag{2}$$

k_1 is the termination constant, k'_1 is the effective termination constant in the sense quoted above, b is a constant. If the exponent of [M] in the general equation describing the rate of polymerization is 0·7, then

$$1 + a - b/2 = 0{,}3 . \tag{3}$$

In media having better dissolving properties, *i.e.* in ethanol, the order with respect to the monomer is a normal one, that is 1·1 (Fig. 1).

In the system triglycol monomethacrylate–triglycol dimethacrylate, too, the dependence of the rate of copolymerization on the concentration of the crosslinking agent has a character similar to the behaviour of the other cases under study (Fig. 2). After the initial stage of the stationary state, in which the rate of copolymerization is independent of the concentration of the crosslinking agent, the gel effect sets in. At this stage, the rate of copolymerization naturally depends on the concentration of the crosslinking agent, similarly to the transition point from the region of the stationary course into the region of the gel-effect. The higher the concentration of the crosslinking agent, the shorter the region of the stationary course of copolymerization, and the higher the rate of polymerization in the gel-effect.

It can be said, therefore, that the polymerization mechanism in the series glycol[1,2], diglycol[1,3] and triglycol monomethacrylate is similar. The difference in the relations between the partial polymerization processes can be ascribed to physical effects. The above kinetic dependences suggest that besides the kinetic course, a similar mechanism can also be assumed in the building of the network in the system triglycol monomethacrylate–glycol dimethacrylate. This assumption is corroborated by two further findings: *a)* The same effect of the chosen crosslinking agent
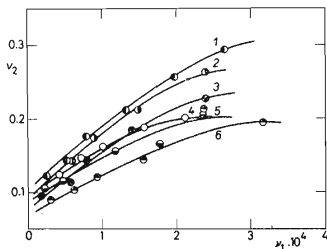

Fig. 3

Dependence of the Equilibrium Degree of Swelling (v_2) of the Copolymers of Triglycol Monomethacrylate with Glycol Dimethacrylate (Curves *1, 2, 3*) and of Triglycol Monomethacrylate with Triglycol Dimethacrylate (Curves *4, 5, 6*) on the Concentration of the Crosslinking Agent (v_1 in mol/cm^{-3})

Water content in the system, %: *1* 10, *2* 20, *3* 40, *4* 10, *5* 20, *6* 40.

(glycol diesters of methacrylic acid) on the equilibrium swelling of gels based on monoesters of the given series (cf. data in ref.[1-3] and Fig. 3). b) Effect of hydrophobic centres on the formation of association crosslinks in the series of hydrophilic copolymers decreases with increasing hydrophilic character of the copolymer. Similarly to the preceding systems[1,2], we modelled the hydrophobic character of the glycol dimethacrylate structural unit by means of the methyl methacrylate unit (copolymerization of triglycol monomethacrylate with methyl methacrylate). The physical crosslinking efficiency of methyl ester (2·2%) was calculated without knowing the interaction parameter for the system under investigation from the ratio of the calculated concentrations
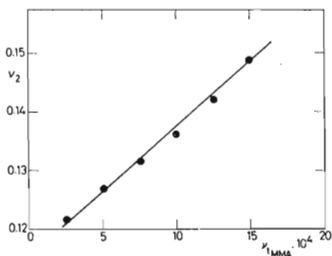

Fig. 4

Effect of the Content of Methyl Methacrylate (v_{IMMA} in mol/cm^{-3}) on the Equilibrium Degree of Swelling of Poly(Triglycol Monomethacrylate–co–Methyl Methacrylate)

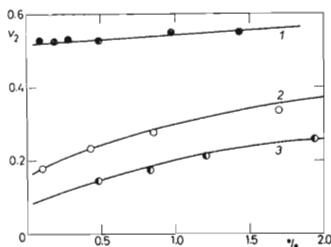Water content in the starting copolymerization mixture: 20%.

Fig. 5

Effect of the Concentration of the Crosslinking Agent (% by Weight) on the Equilibrium Degree of Swelling of the Copolymers of Monomethacrylates with Glycol Dimethacrylate

Monomethacrylate: 1 glycol, 2 diglycol, 3 triglycol.

of comonomers, ν_t (in mol/cm^3 of dry copolymer), corresponding to the same regions of the equilibrium swelling degrees (Δv_2) for glycol dimethacrylate (Fig. 3) and for methyl methacrylate (Fig. 4), that is, as a fraction $84 \cdot 3\cdot3 \cdot 10^{-5}/1\cdot25 \cdot 10^{-3}$ (the crosslinking efficiency of glycol dimethacrylate during copolymerization with diglycol monomethacrylate and at a content of 20% H$_2$O in the starting mixture is 84%)[1]. The association efficiencies of methyl methacrylate in the series of copolymers with glycol, diglycol and triglycol monomethacrylate are $5\cdot5$; $2\cdot4$; and $2\cdot2\%$, respectively.

In the investigated systems of the methacrylic esters of glycols, water is the best solvent for the case of triglycol monomethacrylate (Fig. 5). A comparison of the data obtained proves that in these systems there exist very similar relationships in the process of network formation; moreover, it allows a general conclusion to be drawn from some of the relationships established in the investigation. An important finding should be seen in the low cyclization ability of glycol dimethacrylate, and also in the approximately identical crosslinking efficiency of the crosslinking agents in all the copolymers investigated (under otherwise comparable conditions). The condition to be fulfilled, however, for these conclusions to be valid is that the reaction system ought to be above the second order transition point throughout copolymerization, and the transfer reactions ought to participate to a low extent only.

REFERENCES

1. Kopeček J., Jokl J., Lím D.: J. Polymer Sci. C *16*, 3877 (1968).
2. Kopeček J., Lím D.: J. Polymer Sci. A 1 *9*, 147 (1971).
3. Kopeček J., Lím D.: This Journal, in press.

Translated by L. Kopecká.