

MECHANISM OF THREE-DIMENSIONAL
POLYMERIZATION OF GLYCOL METHACRYLATES. III.*
CONTRIBUTION TO THE POLYMERIZATION KINETICS
OF THE SYSTEM DIGLYCOL MONOMETHACRYLATE-GLYCOL
DIMETHACRYLATES-WATER

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Of all systems leading to the glycol methacrylate gels, the system diglycol monomethacrylate-glycol dimethacrylates-water is best suited for obtaining the basic knowledge about the network formation within a broad range of conversions¹. A detailed picture of the three-dimensional polymerization can be obtained by comparing the kinetic course of the reaction with the polymer structure over the whole range of conversions. We determined, on the basis of the above concept, some further kinetic relationships characterizing the formation of the three-dimensional network in this system. The ratio of reactivities of the pendant vinyl groups and the vinyl groups of the free crosslinking agent were determined over a broad range of conversions; a kinetic proof was also obtained of the different cyclization activity of glycol dimethacrylate compared to diglycol dimethacrylate.

EXPERIMENTAL

Preparation and purification of the starting compounds, the polymerization techniques used and the characterization of polymers have been described in an earlier paper¹. The network density evaluations were made using the Flory-Huggins equation. The interaction parameter was obtained by combining the measurements of the equilibrium swelling and the stress-strain dependence. In the latter measurements, the five-minute modulus was used. In this connection, it should be stressed that the value of this modulus used for the determination of the interaction parameter need not necessarily be an equilibrium one², especially in the case of slightly crosslinked networks and a low degree of swelling, *e.g.* for a system based on glycol monomethacrylate. The time effect in the case of the investigated system based on diglycol monomethacrylate, for which water is a better solvent, and for the regions of the network densities used (Table I) will be small (<5% rel.).

RESULTS AND DISCUSSION

From the experimental results (Table I) and using a procedure described earlier¹, explicit relationships were derived which represent the dependence of the relative concentration of crosslinks (y in %) on conversion ($x \in \langle 0.2; 1 \rangle$) for the system diglycol monomethacrylate-glycol dimethacrylate for 10% and 30% water in the starting mixture,

$$y = 2.13 e^{3.71x} \quad \text{and} \quad y = 2.18 e^{3.64x}, \quad (1a,b)$$

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respectively; owing to the low content of the crosslinking agent and the equality of the copolymerization parameters $r_1 = r_2 = 1$, x can be defined as the total conversion of the system. The not too different character of the above function for both systems under investigation, and of the same function for a system containing 20% water in the starting mixture¹, allow us to assume a low cyclization activity of glycol dimethacrylate in the above range of dilutions of the

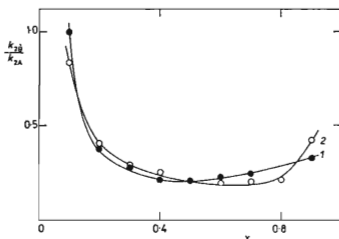


FIG. 1

Dependence of the Ratio of the Rate Constants of Crosslinking (k_{2B}) and Propagation (k_{2A}) on Conversion (x) During Copolymerization of Diglycol Monomethacrylate with Glycol Dimethacrylate

Water content in the starting mixture, %: 1 10; 2 30.

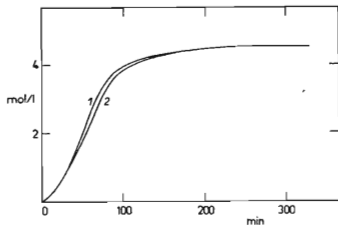
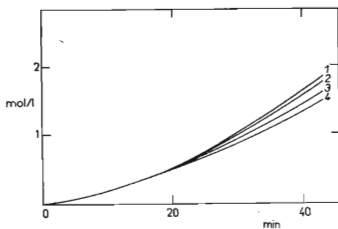


FIG. 2

Effect of the Type of the Crosslinking Agent on the Course of Polymerization of Diglycol Monomethacrylate in the Gel-Effect

Concentration of the components (mol/l): water 12.4; diglycol monomethacrylate 4.5; azo-2,2'-bis(methyl-isobutyrate) $1.1 \cdot 10^{-3}$; diglycol dimethacrylate $5.4 \cdot 10^{-2}$ and $1.05 \cdot 10^{-1}$ (curves 2 and 4); glycol dimethacrylate $5.4 \cdot 10^{-2}$ and $1.05 \cdot 10^{-1}$ (curves 1 and 3).

starting mixture. If, therefore, glycol dimethacrylate does not form small, elastically ineffective cycles, it is possible to calculate the relative concentration of the pendant vinyl groups (\tilde{B} in %) at a certain conversion from the relationship (cf.¹.)

$$\tilde{B} = B_0 x(2 - x) - y, \quad (2)$$

where B_0 is the starting relative concentration of the crosslinking agent (100%).

It is known that after completion of copolymerization a certain number of pendant vinyl groups still remains in the gel; it depends on the lengths of polymer segments and on the structure of the crosslinking agent, mainly on the distance between the double bonds, since it is this distance that affects both the ease of formation of the cycles and the extent of the space in which the pendant vinyl group can move, independently of the motion of the segment to which it is attached. Owing to the limited motion of the pendant vinyl group and the hindering effect of the surrounding polymer molecule, a decrease in the reactivity of the pendant vinyl group^{1,3,4} is observed during copolymerization.

To calculate the change in the reactivity of the pendant vinyl group with conversion, let us consider a simple kinetic scheme of the three-dimensional polymerization (A is the monomer, \dot{R} is the growing polymer radical, B is the crosslinking agent, \tilde{B} is the pendant vinyl group, C is the crosslink):

$$-\frac{d[A]}{dt} = k_{2A}[\dot{R}][A], \quad (3)$$

$$-\frac{d[B]}{dt} = 2k_{2B}[\dot{R}][B], \quad (4)$$

$$\frac{d[C]}{dt} = k_{2\tilde{B}}[\dot{R}][\tilde{B}], \quad (5)$$

$$\frac{d[\tilde{B}]}{dt} = 2k_{2B}[\dot{R}][B] - k_{2\tilde{B}}[\dot{R}][\tilde{B}]. \quad (6)$$

This scheme adequately represents the copolymerization of the system diglycol monomethacrylate-glycol dimethacrylate, since in this case both cyclization and transfer can be neglected, and it can be assumed that $k_{2A} = k_{2B}$. The reactivity ratio of the pendant vinyl group and the free double bond over a wide range of conversions can be characterized by determining the ratio $k_{2\tilde{B}}/k_{2A}$ in terms of equations (3) and (5):

$$\frac{k_{2\tilde{B}}}{k_{2A}} = \frac{\frac{d[C]}{dt}}{\frac{d[A]}{dt}} \cdot \frac{[A]}{[\tilde{B}]}. \quad (7)$$

All quantities on the right-hand side of the equation are experimentally available (for $x > 0.2$): $[A]$ can be read from the kinetic course of polymerization (graphical derivation will then yield $-d[A]/dt$); $[\tilde{B}]$ can be calculated from Eq. (2), and $d[C]/dt$ can then be obtained by graphical derivation of the time dependence of the crosslink formation¹.

TABLE I

Dependence of the Actual Crosslinking Density (ν_e) of Gels on Conversion (x) During Copolymerization (a , b) of Diglycol Monomethacrylate (A) with Glycol Dimethacrylate (B), Initiated with Azo-2,2'-bis(methyl-isobutyrate) (I)

Concentration of components (mol/l), a : $[A] = 5.11$, $[B] = 5.08 \cdot 10^{-2}$, $[H_2O] = 5.55$, $[I] = 1.98 \cdot 10^{-3}$; b : $[A] = 3.96$, $[B] = 5.34 \cdot 10^{-2}$, $[H_2O] = 16.63$, $[I] = 1.37 \cdot 10^{-3}$.

a		b	
x , %	$\nu_e \cdot 10^5$, mol cm $^{-3}$	x , %	$\nu_e \cdot 10^5$, mol cm $^{-3}$
11.34	0.254	10.26	0.373
19.63	1.44	30.21	1.41
50.19	2.95	48.59	2.71
67.66	4.88	69.65	4.76
84.35	9.51	81.42	7.02
98.38	17.0	99.09	15.5

Two causes can contribute to the observed dependence of k_{2B}/k_{2A} on conversion (Fig. 1): namely, a monotonic decrease of the constant k_{2B} during copolymerization due to the reasons described above, and a decrease in the propagation rate constant k_{2A} at the final stage of polymerization. With respect to the small change in the ratio of the above rate constants in the central part of copolymerization, a further influence affecting the constant k_{2B} must be admitted, that is, coalescence of the growing polymer radicals with an inactive polymer containing pendant vinyl groups, which will bring nearer the reaction components, and thus facilitate the crosslinking reaction. This phenomenon would cause an increase in the constant k_{2B} with proceeding conversion; it is in agreement with the experimentally obtained exponential dependence of the concentration of crosslinks on conversion.

The above results hold for the case when glycol dimethacrylate is used as the crosslinking agent, and the cyclization reaction can be neglected¹. For dimethacrylate prepared from diglycol and triglycol, different crosslinking activities were established by determination of the equilibrium swelling; this was explained in terms of different cyclization abilities¹ in accordance with what is generally known about the cycle formation. The rate of copolymerization in the region of the gel-effect is most affected by the rate of crosslink formation, because the formation of a crosslink through the reaction of a growing polymer radical with a vinyl group pendant on the polymer chain will contribute to an increase in the viscosity of the medium, and thus to a drop in the termination constant, much more than a single propagation or cyclization step (ref.¹, Fig. 11).

The experimental proof of the above assumption is shown in Fig. 2. The copolymerization of diglycol monomethacrylate with glycol dimethacrylate in the region of the gel-effect occurs faster than the copolymerization of diglycol monomethacrylate with diglycol dimethacrylate (Fig. 2a). The curves, which have different slopes in the region of the gel-effect, meet at the final slow step of copolymerization (Fig. 2b).

The method described in the present paper can be used as a rapid qualitative method for determination of the crosslinking activity of the crosslinking agents having similar structures in those cases in which the copolymerization parameters can be regarded as identical.

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**STUDY ON THE BEHAVIOUR AND THE REACTIVITY
OF SOLUTIONS OF COMPLEX HYDRIDES. I.
CONTRIBUTION TO THE MECHANISM OF THE REDUCTION
OF KETONES WITH A BENZENE SOLUTION
OF SODIUM DI(2-METHOXYETHOXY)ALUMINUM HYDRIDE***

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In connection with our studies of alkoxyaluminum hydrides of alkali metals stable sodium di(2-methoxyethoxy)aluminum hydride, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, has been prepared^{1,2}. Its reducing capacity has been studied in a number of papers³⁻¹¹ from which it followed that in the majority of cases it is comparable with the reducing capacity of lithium aluminum hydride. In this respect it is not without interest to compare the mechanisms of the reductions with both agents. In addition to this the solubility of the new reagent in benzene (in which it is present in monomeric form¹² at the boiling point of the solvent enables us for the first time to follow the reductions with complex hydrides in solvents without donor atoms. For our study we investigated the course of the reduction of ketones which can give two epimeric alcohols.

Our procedure was similar to that of Haubenstock and Eliel¹³ who studied the reduction of 3,3,5-trimethylcyclohexanone using a series of ethereal and tetrahydrofuran solutions of lithium aluminum hydride and of alkoxyhydrides derived from it, $\text{LiAlH}_{4-n}(\text{OR})_n$, where R are primary, secondary, and tertiary alkyls. From the comparison of the ratios of epimeric alcohols obtained by reduction with the mentioned three types of alkoxyhydrides and the ratios of epimers found after the reduction with LiAlH_4 alone, the authors derived a "disproportionation" mechanism of the reduction of ketones, based on the assumption of the instability of alkoxyhydrides $\text{LiAl} \cdot \text{H}_{4-n}(\text{OR})_n$ with secondary R, which were considered earlier as possible intermediary steps of the reduction of ketones¹⁴.

In our work we also employed 3,3,5-trimethylcyclohexanone as a representative of ketones of cyclohexanone series with an only slightly sterically hindered keto group (caused by the axial methyl group in the position 3), in which the stereochemical course of the reduction may be

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