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The autocatalytic model of photopolymerization of dimethacrylates

RAPID COMMUNICATION

Summary — The aim of the work was to analyze photopolymerization kinetics of a series of homologous alkylene dimethacrylates according to the autocatalytic model. The model parameters *k*, *m* and *n* (where *k* is the rate constant at temperature *T*, *p* is fractional conversion after time *t*, *m* is the autocatalytic exponent, and *n* is the reaction order exponent) were determined for the polymerization of six monomers under argon at six temperatures (40, 50, 60, 70, 80, and 90°C). The investigation of a series of dimethacrylates differing only in the number of -CH_2- groups in the spacer group allowed the effect of the length of the monomer molecule on these parameters to be studied. The experimental method was based on differential scanning calorimetry (DSC). The parameters *k*, *m* and *n* were calculated from a best fit between model prediction and data points of the experimental curves polymerization rate versus conversion degree. Statistical analysis showed a very good fit of the model to the experimental data. It was found that *k* values increase with the number of -CH_2- groups in the monomer molecule and with the polymerization temperature. The values of *m* and *n* show a tendency to decrease with increasing temperature. The values of the parameters for all the monomers lie in the range of 0.031—0.054 s^{-1} (*k*), 0.44—0.70 (*m*) and 1.44—1.75 (*n*).

Key words: photopolymerization, dimethacrylates, autocatalytic model.

The autocatalytic effect occurs usually due to formation of some intermediate species, which markedly accelerate the reaction. For instance, the curing process for epoxy-amine thermoset resins is autocatalyzed by hydroxyl groups formed in the reaction. Processes of this type are often described by the phenomenological model (eq. 1):

$$R_p = k \cdot p^m \cdot (1 - p)^n \qquad (1)$$

where: R_p *is the polymerization rate, k is the rate constant at temperature T, p is the fractional conversion after time t, m is the autocatalytic exponent, and n is the reaction order exponent.*

The autocatalytic model has been used extensively and has been shown to predict the cure of thermoset resins accurately [1].

Some attempts have also been made to apply eq. (1) to describe the polymerization of multifunctional monomers. The reaction kinetics during propagation of a crosslinking process is from the beginning dominated by the autoacceleration [2]. In the case of crosslinking polymerization the increase in the polymerization rate is caused by restricted diffusion of the reactive chain ends connected with the network being formed [3]. As the result, the shape of the polymerization rate vs. conversion curves for autoaccelerated processes is the same as that in the autocatalytic reactions; thus eq. (1) can also be applied to describe the crosslinking polymerization. In eq. (1), p^m represents, in a phenomenological way, the effects of the different constraints below the vitrification regime. The three kinetic parameters — *k*, *m* and *n* — take into account all the effects that influence the reaction rate, such as the specific reactivity of the functional groups, the autoacceleration or the gel effect, and the topological or structural effects [4].

Only a limited number of works have been devoted to the description of the photoinitiated crosslinking polymerization by the autocatalytic model [3, 5—7], all of them were based on DSC measurements.

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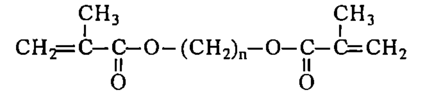
The aim of the work was to analyze the photopolymerization kinetics of a series of homologous dimethacrylates of the formula (I) according to the autocatalytic model.



$$CH_2{=}\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-(CH_2)_n-O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{C}{=}CH_2$$

(I)

n = 2, 4, 5, 6, 8, 10

The model parameters *k*, *m* and *n* were determined for the photopolymerization at six polymerization temperatures (40, 50, 60, 70, 80, and 90°C). The investigation of the series of dimethacrylates differing only in the number of -CH_2- groups in the spacer group allowed the effect of the length of the monomer molecule on these parameters to be studied.

EXPERIMENTAL

The monomers used were: ethane-1,2-diol dimethacrylate (EDM, n = 2), butane-1,4-diol dimethacrylate (BDM, n = 4), pentane-1,5-diol dimethacrylate (PDM, n = 5), hexane-1,6-diol dimethacrylate (HDM, n = 6), octane-1,8-diol dimethacrylate (ODM, n = 8) and decane-1,10-diol dimethacrylate (DDM, n = 10). The monomers were commercial products (EDM, BDM and HDM, Aldrich) or were synthesized (PDM [8], ODM, and DDM).

Reaction rate profiles and conversions were determined by differential scanning photocalorimetry (DSC 605M instrument, UNIPAN-TERMAL, Warsaw) under isothermal conditions. The polymerization was initiated by 366 nm light from a medium - pressure Hg lamp (incident light intensity 1.8 mW/cm^2) and by 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (Irgacure 369, Ciba-Geigy) at conc. of 0.01 M. Irradiation was carried out in argon atmosphere.

Although eq. (1) has a functional shape similar to the DSC curves, it predicts a final degree of reaction equal to 1 . Because crosslinking systems usually do not reach full cure, *p* in eq. (1) denotes the relative conversion and for calculations it was taken as the ratio:

$$p = p_a/p^f \tag{2}$$

where: p_a *is the actual conversion (expressed as fractional conversion of double bonds) and* p^f *is the final conversion reached under given polymerization conditions.* R_p values were calculated in the same way.

The model parameters were determined after linearization of eq. (1). For calculations Linear Least Square Method was used. Statistical importance of the model was tested using F-Snedecor function.

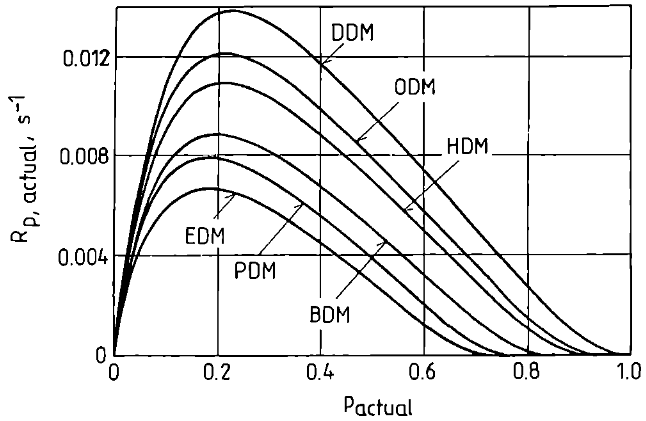


Fig. 1. Actual polymerization rate ($R_{p,actual}$) vs. actual double bond conversion (p_{actual}) curves for investigated monomers at 50°C

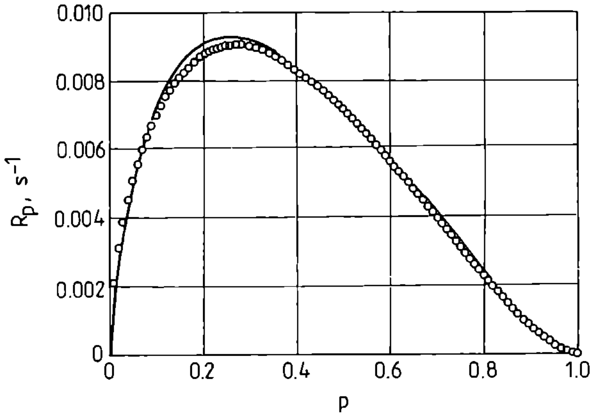


Fig. 2. Relative polymerization rate (R_p) as a function of relative conversion (p) for ethylene glycol dimethacrylate polymerization in Ar at 50°C. Solid line, experimental curve; circles, calculated curve

RESULTS AND DISCUSSION

Exemplary actual polymerization rate vs. actual double bond conversion curves for investigated monomers at 50°C are shown in Fig. 1. As expected, both the maximum polymerization rate R_p^{max} as well as p^f values increase with the length of the spacer group between the two unsaturations. The values of these parameters increase also with polymerization temperature.

The parameters *k*, *m* and *n* were calculated from a best fit between model prediction and data points of the experimental polymerization rate versus conversion degree curves (Fig. 2). Statistical analysis showed very good fit of the model to the experimental data.

Correlation coefficient was in the range of 0.9814—0.9999 and F-Snedecor function was >10 at the critical value F = 2.70. Thus, the model may be successfully applied to the description of the polymerization course of dimethacrylates.

The results of calculations (*k*, *m* and *n* values) as a function of polymerization temperature are shown in Figs. 3, 4, and 5. The values of the parameters for all the monomers lie in the range of 0.031—0.054 s^{-1} (*k*), 0.44—0.70 (*m*) and 1.44—1.75 (*n*). The plots in Figures

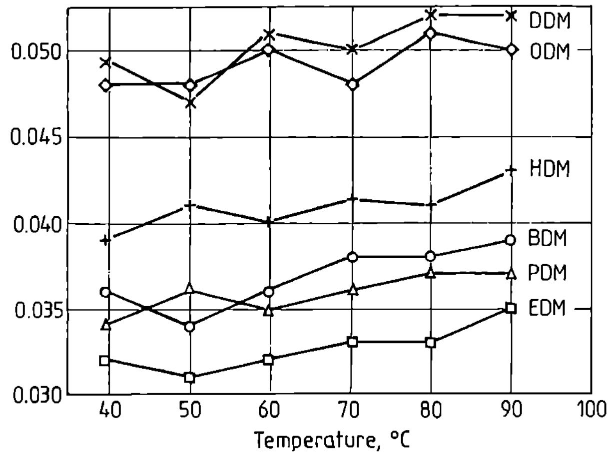


Fig. 3. Rate constant k as a function of temperature for the polymerization of the monomers investigated

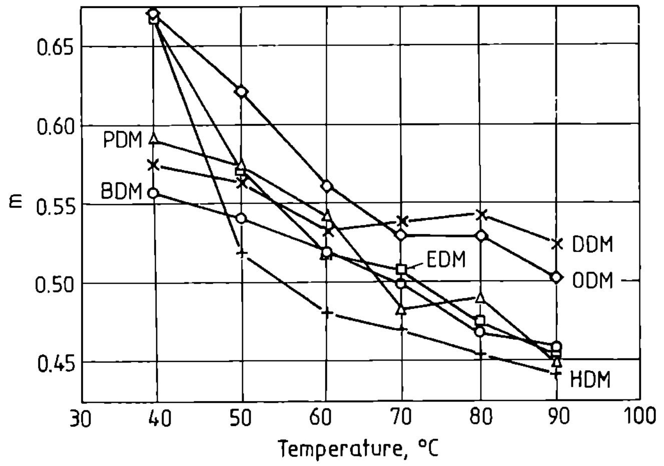


Fig. 4. Autocatalytic exponent m as a function of temperature for the polymerization of the monomers investigated

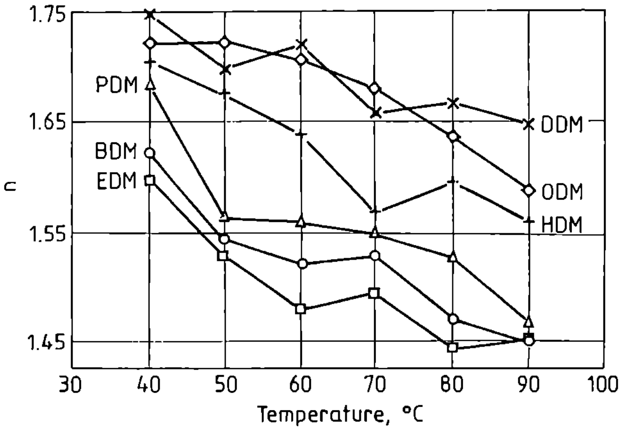


Fig. 5. Reaction order exponent n as a function of temperature for the polymerization of the monomers investigated

clearly indicate the dependence of all the parameters of the model on temperature. The increase in k with temperature is in agreement with the general dependence of rate constants expressed by an Arrhenius relation. The m and n exponents seem to decrease when the polymerization temperature is raised. However, the exponents determined for the photopolymerization of ethoxylated bisphenol A dimethacrylate (m = 0.8, n = 2) [5], although similar in values to those determined in our study, were found to be independent of temperature. On the other hand, a decrease in values of the discussed parameters was observed in another work for the photopolymerization of six analogous di(meth)acrylates [3].

Because the autocatalytic effect is caused by network formation and resulting restricted diffusion of macroradicals, an increase in network mobility at higher temperatures should reduce the dependence of the polymerization rate on network density and monomer concentration. This, in turn, should lead to a decrease in n and m exponents with an increase in temperature, which was really observed.

Considering the effect of the length of the spacer group on k value it was found that k increased with the number of -CH_2- groups in the monomer molecule. This can be attributed to a reduction of network density due to elongation of the distance between crosslink points. The resulting greater mobility of the network facilitates the propagation.

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