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## Copolymerization of dodecyl methacrylate with oxyethylene glycol dimethacrylates: determination of reactivity ratios

### RAPID COMMUNICATION

**Summary** — The work presents the results of determination of reactivity ratios for vinyl/divinyl systems based on dodecyl methacrylate and four oxyethylene glycol dimethacrylates. Various methods (based on terminal model and penultimate effect) were used for calculation of experimental results. The experimental data were obtained by gas chromatography (determination of unreacted monomers in the feed) and by NMR analysis of the soluble copolymer. It was found that dimethacrylates were preferentially built into the copolymer chain. These results were in good agreement with quantum-mechanical calculations based on the analysis of heats of formation of short-chain oligomers.

**Key words:** copolymerization, dimethacrylates, monomethacrylates, reactivity ratios, terminal model, penultimate effect, quantum-mechanical calculations.

Polymerization of multifunctional monomers leads to the formation of highly crosslinked insoluble products. The resulting polymer network is heterogeneous due to microgel formation. The density of the network can be regulated by an addition of monovinyl monomer. Decrease in a crosslinking density allows to reach higher conversion of double bonds and to reduce the polymerization shrinkage. However, reduction of crosslinking density by copolymerization with monovinyl monomer can lead to an increase in heterogeneity due to a compositional drift associated with different reactivities of comonomers. The more heterogeneous is a material, the more likely it will show a significantly weaker structure in some regions, potentially causing premature failures [1]. Thus, the knowledge of the reactivity ratios for monovinyl/divinyl systems is very important to predict the final product properties.

There are many methods of estimation of reactivity ratios, all of them based on Mayo—Lewis equation and classified as differential or integral ones [2]. The corresponding equations and solution methods are linear or

non-linear. Currently, the non-linear methods are recommended [3]. Although a great number of works was devoted to determination of reactivity ratios in various systems, only a limited number of them considered monovinyl/divinyl systems [4—6].

The aim of this work was to determine the reactivity ratios of dodecyl methacrylate and four oxyethylene glycol dimethacrylates, differing in oxyethylene segments' lengths, using various calculation methods. Additionally, the preferences of the individual monomers concerning an addition to various terminal units of the copolymer chains were estimated by quantum-mechanical calculations, based on the analysis of heats of formation of short-chain oligomers.

### EXPERIMENTAL

#### Materials

- All the monomers as follows:
- dodecyl methacrylate (DDM),
  - ethylene glycol dimethacrylate (EGDM),
  - di(ethylene glycol) dimethacrylate (DEGDM),
  - tri(ethylene glycol) dimethacrylate (TEGDM),
  - tetra(ethylene glycol) dimethacrylate (TtEGDM),

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were purchased from Aldrich Company and purified by column chromatography before use.

2,2-Dimethoxy-2-phenylacetophenone used as an initiator of copolymerization was delivered by Ciba Speciality Chemicals.

### Copolymer synthesis and testing

The copolymerization was induced photochemically at 40 °C with the 365 nm light of 1 mW/cm<sup>2</sup> intensity in the presence of 2,2-dimethoxy-2-phenylacetophenone (1 wt. %).

For gas chromatography investigations, 10 mg samples were irradiated for a time needed to obtain ≤ 5 % conversion of double bonds (as estimated by DSC method) and after irradiation immediately treated by chloroform to extract the unreacted monomers. The soluble polymer was precipitated using methanol and unreacted monomers were analyzed by GC in the filtrate.

In the case of NMR investigation, 0.5 g samples were polymerized to conversion also ≤ 5 wt. % and the soluble copolymer was analyzed.

### COMPUTATION METHODS

The reactivity ratios were estimated using ProCop computer program [2]. Two methods based on terminal model, Kelen—Tüdös (KT, linear), Tidwell—Mortimer (TM, nonlinear), and a method taking into account penultimate effect (PTM) were used.

The probability of formation of short oligomeric copolymer chains, differing in the number and the position of two types of monomer units, was estimated on the basis of geometry optimization, which enabled calculation of the reaction enthalpy ( $\Delta H_r$ ) from the following relation:

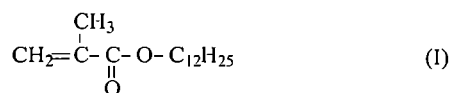
$$\Delta H_r = \Delta H_n - (\Delta H_{n-1} + \Delta H_u) \quad (1)$$

where:  $n$  — number of units,  $\Delta H_n$  — heat of formation of the oligomer,  $\Delta H_u$  — heat of formation of the terminal unit.

Calculations were performed by semiempirical method PM3 using HyperChem 7.0 computer program. The lower  $\Delta H_r$  value, the more probable is the oligomer structure consisting of a given number of units.

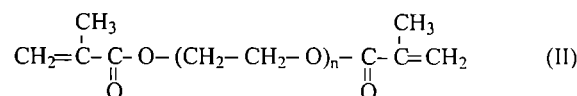
### RESULTS AND DISCUSSION

DDM [Formula (I)] was copolymerized with four dimethacrylates [Formula (II)].



The calculated monomer reactivity ratios are given in Table 1.

In almost all cases (one exception:  $r_2$  close to 1 obtained by TM method for DDM/DEGDM system)  $r_2$  va-



$n = 1$  — EGDM  
 $n = 2$  — DEGDM  
 $n = 3$  — TEGDM  
 $n = 4$  — TtEGDM

Table 1. Reactivity ratios of DDM and ethylene glycol dimethacrylates, determined by various calculation methods

Composition	Calculation method	$r_1$ (DDM)	$r_2$ (dimethacrylate)	Standard deviation · 10 <sup>3</sup>
DDM/EGDM	KT	0.04920	1.45110	123.500
	TM	0.16200	2.81530	110.360
	PTM	$r_{11} = 0.30902$ $r_{21} = 0.06192$	$r_{22} = 2.05309$ $r_{12} = 3.40448$	105.260
DDM/DEGDM	KT	0.40380	1.02400	38.000
	TM	0.36070	0.92700	36.980
	PTM	$r_{11} = 0.85886$ $r_{21} = 0.06389$	$r_{22} = 2.44437$ $r_{12} = 0.15267$	32.430
DDM/TEGDM	KT	0.26520	2.12060	74.350
	TM	0.20930	1.59070	70.558
	PTM	$r_{11} = 0.03786$ $r_{21} = 0.21272$	$r_{22} = 4.45405$ $r_{12} = 0.30717$	68.290
DDM/TtEGDM	KT	0.25700	1.42520	98.360
	TM	0.26590	1.21330	90.010
	PTM	$r_{11} = 47.91000$ $r_{21} = 0.00060$	$r_{22} = 242.88900$ $r_{12} = 0.00267$	68.255

lues are higher than 1 and  $r_1$  values are lower than 1, suggesting higher activity of divinyl monomers added to the copolymer chain. This in turn indicates that the polymer formed at the beginning of the reaction will be more densely crosslinked than that one formed in the final reaction stages. In calculations carried out in this work the fact that one of the two comonomers has two double bonds was not taken into account (this approach is more popular [5, 6]) although some works appeared, in which monomer functionality higher than two was introduced to the expression describing the reactivity ratios [4, 7].

The composition diagrams of DDM/DEGDM and DDM/TEGDM systems are presented in Fig. 1 and 2, respectively. The fitted curves suggest that the data obtained for DDM/TEGDM system (and DDM/TtEGDM, not shown here) are better described by PTM model (taking into account that units before the last one may affect the reactivity of a chain radical), whereas in the case of two shorter dimethacrylates the both models, *i.e.* ultimate one (assuming that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain) and PTM give very similar results.

The results of calculations of reaction heats of DDM/TtEGDM system are given in Table 2 and sche-

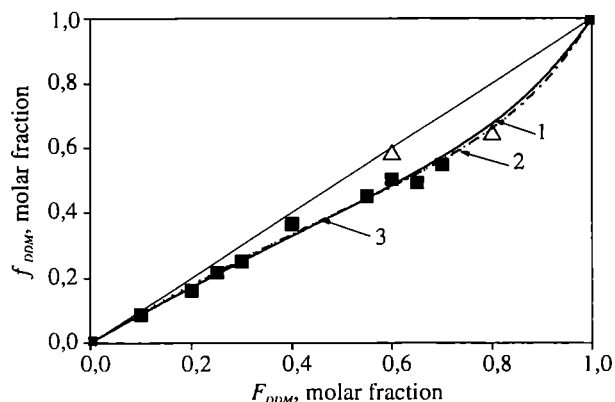


Fig. 1. Copolymer composition ( $f$ ) versus comonomer feed composition ( $F$ ) for DDM/DEGDM system; ■ — experimental data from gas chromatography,  $\Delta$  — experimental data from NMR, lines represent theoretical curves calculated from reactivity ratios estimated by KT (1) and TM (2) methods and by PTM (3) model

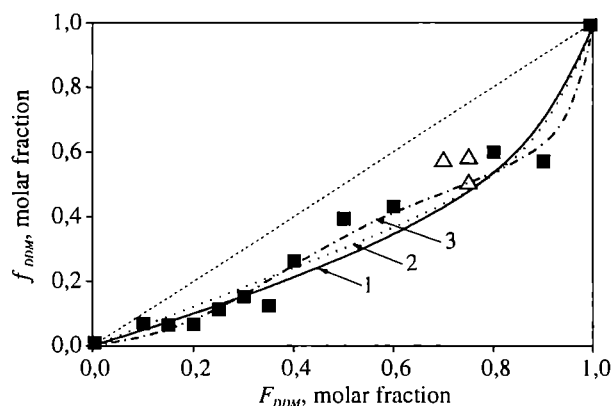


Fig. 2. Copolymer composition ( $f$ ) versus comonomer feed composition ( $F$ ) for DDM/TEGDM system; denotations as in Fig. 1

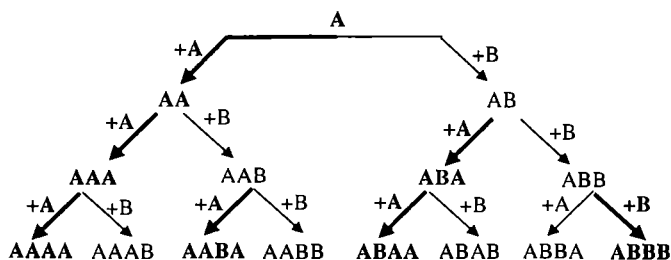


Fig. 3. Possible events of comonomer additions. Thick lines indicate the preferential addition of the comonomer to the copolymer terminal unit, A and B denote TtEGDM and DDM, respectively

Table 2. Heats of reactions ( $\Delta H_r$ ) and mole fractions of individual oligomers, calculated by quantum-mechanical methods for the system DDM/TtEGDM; denotations as in Fig. 3

Structure	$\Delta H_r$ , kcal/mol	Molar fraction <sup>*)</sup>
AA	-19.2576	0.55400
AB	-19.0375	0.44600
AAA	-14.8902	0.25123
ABA	-13.7376	0.25093
AAB	-14.1557	0.25067
ABB	-4.9475	0.24715
AAAA	-11.3117	0.12281
AAAB	-11.0454	0.12276
ABAA	-9.6022	0.12220
ABAB	-7.6690	0.12183
AABA	-13.7812	0.12316
AABB	-13.1772	0.12304
ABBA	-20.3190	0.12259
ABBB	-21.9450	0.12291

<sup>\*)</sup> Calculated from Boltzmann distribution.

matically shown in Fig. 3. Thick lines indicate the preferential addition of the comonomer to the copolymer terminal unit. The results show that in the most cases  $\Delta H_r$  values are lower for the addition of dimethacrylate than those for DDM, independently on the nature of terminal unit in the copolymer chain, which the addition occurs to. Thus, the results of theoretical calculations are in good agreement with those obtained directly from reactivity ratios determinations.

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