Calorimetric Study of Photopolymerisation of Divinyl Monomers

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SUMMARY: Isothermal differential scanning calorimetry (photocalorimetry) enables real-time measurements of rates of polymerisation as functions of irradiation time to be made. Since it is possible to stop initiation at any point in a reaction (by cutting off the light) and to monitor the dark reaction, this method has been widely used for determinations of the (apparent) rate constants of polymerisation of multifunctional monomers at various degrees of double bond conversion. The work reported here presents the results of photocalorimetric studies of polymerisation kinetics of six related acrylates and methacrylates. Two main topics are discussed: the effects of sulphide and ether groups present in the monomers on network formation, and the determination of polymerisation rate constants according to three termination models (monomolecular, bimolecular and mixed).

Introduction

UV-irradiation in the presence of a suitable photoinitiator is one of the most efficient methods for generating highly crosslinked polymers from multifunctional monomers. The industry today is dominated by acrylate and mathacrylate chemistry. Because of the importance of free-radical photopolymerisations of multifunctional monomers and the effects of polymer structure on material properties, it is necessary to study the influence of reaction conditions and monomer structure on the polymerisation kinetics.

Differential scanning calorimetry is the most widely used real-time technique for studying photocuring kinetics. When used under isothermal condition to follow a photo-induced polymerisation, it is often called photocalorimetry. It measures directly the heat flow, which is proportional to the rate of polymerisation (R_p), as a function of irradiation time (t). Thus, R_p (in mole $l^{-1}s^{-1}$) at any point in the reaction can be derived from the heat flow using equation 1 provided that the standard heat of polymerisation is known for the monomer concerned:

$$R_p = \frac{dH}{dt} \cdot \frac{M}{H_0 \cdot n} \qquad (1)$$

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where dH/dt is the heat flow in $J \cdot mol^{-1} \cdot s^{-1}$, M is the monomer concentration in $mol \cdot l^{-1}$, H_0 is the standard heat of polymerisation in $J \cdot mol^{-1}$, and n is the number of double bonds per monomer molecule.

For acrylates H_0 is usually in the range of 78 – 86 $kJ \cdot mol^{-1}$ and for methacrylates 56-58 $kJ \cdot mol^{-1}$. A typical (corrected) photo-DSC trace of the polymerisation of a multifunctional monomer is shown in Fig. 1a.

The total amount of heat evolved is related to the final degree of conversion and the degree of conversion at any conversion (p) can be obtained as the area under the dH/dt curve (Fig. 1b). Photocalorimetry is very sensitive to very small changes in the reaction rate and, thus, it is particularly suitable for the investigation of polymerisation kinetics.

The kinetics of network formation are complicated by factors not observed in linear polymerisation.[1)] One of them is the almost immediate onset of autoacceleration, causing the polymerisation rate to increase with time from the very beginning of the reaction (Fig. 1a). The important parameters characterizing the kinetic curves are: R_p^{max}: the maximum polymerisation rate, p_{Rm} the conversion at R_p^{max}; t_{Rm} the time to R_p^{max}; and p^f the final double bond conversion that can be reached under given reaction conditions.

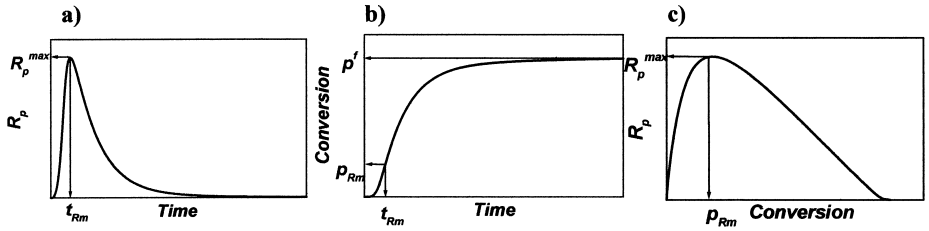


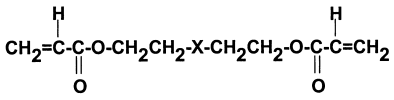
Fig. 1: Typical dependences of polymerisation rate, R_p, and double bond conversion, p, vs. irradiation time and R_p vs. p for the polymerisation of multifunctional monomers.

The results of photocalorimetric investigations into polymerisation kinetics of diacrylates and dimethacrylates are presented in this work. Two main topics are discussed: (i) the effects of sulphide and ether groups introduced to the monomers on network formation; (ii) the determination of polymerisation rate constants.

Experimental Part

All results were obtained using a differential scanning calorimeter (DSC 605, Unipan Termal, Warsaw) equipped with a lid specially designed for photochemical measurements. The sampling density was 0.2 s. The formulations (10 mg) were polymerised in 6.8 mm diameter open aluminium DSC pans. An empty DSC pan was used as reference. When a polymerisation was carried out in an inert atmosphere, the sample was allowed to equilibrate in the apparatus under Ar of special purity for 10 min at the chosen polymerisation temperature. The polymerisation was initiated by a 110 W medium pressure mercury lamp equipped with a glass filter (310-400 nm with λ_{max}=366 nm)

The monomers used were:



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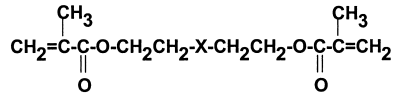

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X = S: 2,2'-thiodiethyl diacrylate **TEDA (1)** and dimethacrylate **TEDM (2)**

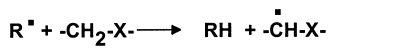
X = O: 2,2'-oxydiethyl diacrylate **OEDA (1)** and dimethacrylate **OEDM (2)**

X = CH_2: pentane-1,5-diol diacrylate **PDA (1)** and dimethacrylate **PDM (2)**

The Effects of Heteroatoms

The presence of a heteroatom (O or S) in the monomer molecule markedly affects network formation. Heteroatom-containing monomers polymerise faster and to higher conversion than their hydrocarbon analogues. The effect is much more pronounced in air and is considerably stronger for the sulphide than for the ether group (Fig. 2).

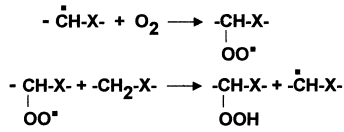
The effects of the heteroatom result mainly from the ability of CH_2 group attached to S or O to donate hydrogen:[2-5)]



(2)

where X is the heteroatom (O or S), $R^{\bullet}$ is a macroradical, peroxy radical or initiator–derived radical. Reaction (2) is faster for sulphur-containing monomers than for oxygen-containing ones. This was confirmed by theoretical calculations[5)] and experimental data[6)]. In air, reaction

(2) leads to a significant reduction of oxygen inhibition due to the accelerated consumption of dissolved and diffusing oxygen in the chain reaction process:



a) b)

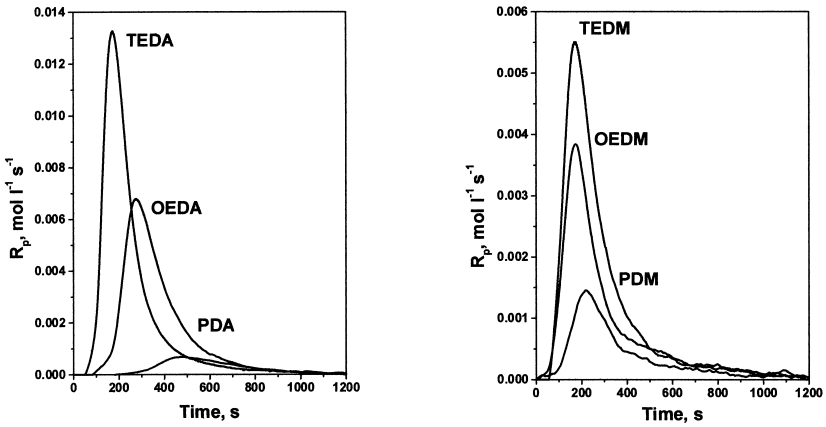


Fig. 2: Time – rate-of-polymerisation curves in air at 50°C: a) diacrylates, initiator: 1-benzoyl-oxycyclohexanol, 0.04 M (ref.[2]); b) dimethacrylates, initiator: 1-benzoyloxycyclohexanol, 0.01 M (ref.[3]).

The reduction of oxygen inhibition effect is the main reason for high polymerization rates and high conversion of heteroatom-containing monomers.

Reaction (2) leads to enhanced crosslink density due to grafting. It also introduces some mobility to radical sites attached to the network. These effects influences the kinetics, especially in the absence of oxygen. Although crosslinking accelerates polymerisation at low conversions, it ultimately restricts the diffusion of macroradicals and monomer at high conversions. For this reason, the final conversion degree depends mainly on the network mobility. Relatively high conversions observed for S and O containing monomers may be caused by the higher flexibilities of the diacrylate or dimethacrylate spacer groups due to

lower barriers to rotation of the carbon – heteroatom bond as compared with that for the methylene group. This applies especially to the C-S bond.
The beneficial effect of heteroatoms has also been observed in formulations using TEDA or OEDA with an epoxyacrylate monomer.[5)]

Determination of Polymerisation Rate Constants

Since it is possible to stop initiation at any reaction point (by cutting off the light) and to monitor the dark reaction, photocalorimetry has been widely used for determination of the (apparent) rate constants of the polymerisation of multifunctional monomers at various degrees of double bond conversion.[1)]

Determination of the rate constants requires an assumption concerning the reaction mechanism and the related kinetics model describing polymerisation in the stationary (during illumination) and non-stationary (after stopping the illumination) conditions. One of the most important processes occurring during the polymerisation of multifunctional acrylates is radical trapping, leading to an additional termination mechanism, i.e., *monomolecular termination*, a first order process occurring simultaneously with the usual bimolecular reaction between two macroradicals (*bimolecular termination*). Thus, the termination process may be considered to occur according to one of three possible termination mechanisms,[7)] monomolecular (when all radicals become trapped), bimolecular (usual termination reaction between two macroradicals), and mixed (simultaneously occurring monomolecular and bimolecular processes). By combining equations describing these processes with an expression for the polymerisation rate in the absence of initiation, we obtain three *termination models* describing the polymerisation in the dark:[7-9)]

-monomolecular termination model (*model I*):

$$-\ln(1-p_d)=\frac{k_p}{k_t^m}[P^\bullet]_0\cdot\left(1-\exp(-k_t^m t)\right) \tag{5}$$

-bimolecular termination model (*model II*):

$$-\ln(1-p_d)=\frac{1}{2}\frac{k_p}{k_t^b}\ln\left(1+2\cdot[P^\bullet]_0\cdot k_t^b\cdot t\right) \tag{6}$$

- mixed termination model (*model III*):

$$-\ln(1-p_d)=\frac{1}{2}\frac{k_p}{k_t^b}\ln\left(1+2\cdot[P^\bullet]_0\cdot\frac{k_t^b}{k_t^m}\cdot(1-\exp(-k_t^m t))\right) \quad (7)$$

The meanings of the symbols are: k_p: propagation rate constant, k_t^b: bimolecular termination rate constant k_t^m: monomolecular termination rate constant, $[P^\bullet]_0$: concentration of macro-radicals at the beginning of dark period, t: time from the start of dark reaction, and p_d: degree of double bond conversion in the dark. The kinetic parameters: k_t^m/k_p and k_t^b/k_p can be calculated from these models.

Model II in its simplified, partly integrated form, has been used widely for the determination of rate constants.[1,10] The individual rate constants can be evaluated by using additionally the steady-state equations for the polymerisation rate with termination assumed to be monomolecular, bimolecular, or of mixed type:

monomolecular termination: $$R_p^b=\frac{k_p}{(k_t^b)^{1/2}}[M]\phi^{1/2} \quad (8)$$

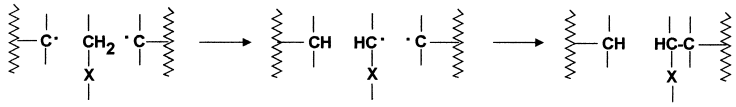
bimolecular termination: $$R_p^m=\frac{2k_p}{k_t^m}[M]\phi \quad (9)$$

mixed termination:[9] $$R_p^{mix}=\frac{k_p}{4k_t^b}[M]\{[(k_t^m)^2+16\phi k_t^b]^{1/2}-k_t^m\} \quad (10)$$

where $\phi = I_a \cdot \Phi$; I_a is the absorbed light intensity and Φ is the quantum yield of initiation. In our work we used a statistical analysis (based on F-Snedecor test) to find the model that best fits experimental data.

Using models I – III we compared the photopolymerization kinetics of TEDM and OEDM at R_p^{max} [7] (Table 1). The statistical analysis showed that the experimental data were best reproduced by the mixed termination model (model III). Looking at the values of parameters listed in Table 1 for this model, one can see that during polymerisation of the sulphur-containing monomer, radical-trapping occurred to much lesser extent in comparison to the oxygen-containing one and the contribution of bimolecular reaction to the overall termination process was greater.

One of the reasons of different behaviour of these monomers may be the extent of chain transfer. Such reaction enhances the mobility of radical sites and is faster in the presence of a sulphide group:



X = O or S

Table 1: Kinetic parameters at R_p^{max} calculated from models I-III for OEDM and TEDM polymerisations in Ar at 40°C. Incident light intensity (I_0): 1.4 mWcm^{-2}, initiator: 2,2-dimethoxy-2-phenylacetophenone (DMPA) 0.02M (ref.[7]).

Model	Parameter	TEDM	OEDM
I	$k_t^m \times 10^2$ /s^{-1}	0.696	1.794
II	k_t^b / k_p	3.2	8.0
III	$k_t^m \times 10^2$ /s^{-1}	0.231	1.518
	k_t^b / k_p	2.1	1.1

Taking OEDM as a model monomer, we have evaluated for the first time for each termination model[9] the rate constants in relation to the degree of conversion of double bonds. The statistical analysis suggested that starting from ca. 10% double-bond conversion, the mixed termination dominated. Below that conversion, the results of the statistical analysis were ambiguous.

The results obtained using model II are shown in Fig. 3. One can see a typical conversion dependence of the rate constants: a rapid drop, a plateau region and another drop of k_t^b, and an almost constant k_p value up to high conversions[1]. The dominating effect of diffusion on the termination mechanism occurs between ca. 15–50% double-bond conversion. It is worth noting that in this model all the termination processes, including monomolecular ones, are represented by k_t^b.

The rate constants calculated from model I (Fig. 4) show a similar behaviour to those in model II. k_t^m decreases with increasing conversion, suggesting that, under continuous

initiation, all the termination processes, represented by k_t^m, slow down as the reaction proceeds.

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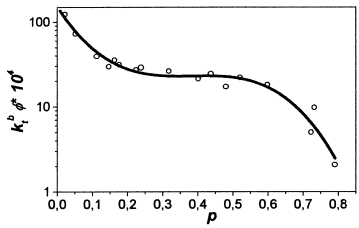

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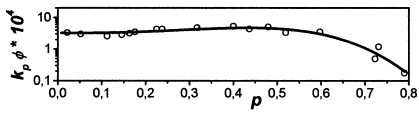
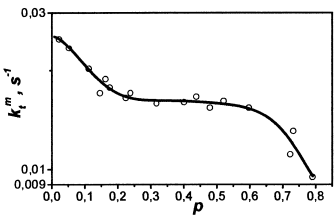


Fig. 3: The apparent rate constants for model II vs. degree of double bond conversion for OEDM polymerisation at 40^{0}C in Ar; DMPA 0.03M, I_0 = 1.3 mW·cm^{-2}: a) $k_t^b \phi$, b) $k_p \phi$. The rate constants are shown regardless of the model that according to statistical analysis yields the best fit (from ref.[9]).

a)



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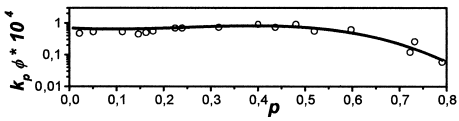
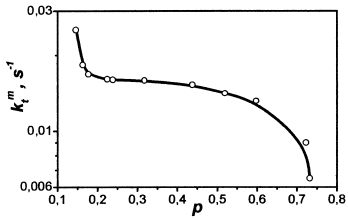


Fig. 4: The apparent rate constants for model II vs. degree of double bond conversion for OEDM. Conditions as in Fig. 3; a) k_t^m; b) $k_p \phi$. The rate constants are shown regardless of the model that, according to statistical analysis, yields the best fit (from ref.[9]).

a)



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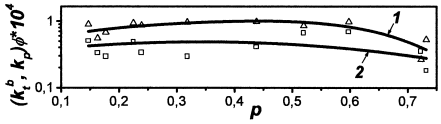

Fig. 5: The apparent rate constants for model II vs. degree of double bond conversion for OEDM. Conditions as in Fig. 3; a) k_t^m; b) $k_p \phi$ (1) and $k_t^b \phi$ (2). The rate constants are shown only for the measurements best reproduced by the model (from ref.[9]).

The determination of rate constants from model III becomes feasible only when this model is shown by statistical analysis to give the best fit to experimental data (Fig. 5). Thus, the initial range of conversion, where the kinetic constants change very quickly, has to be excluded. It can be seen that the mixed-type model (III) yields results that are consistent with the relationships obtained using models I and II. The low $k_t^b\phi$ values, lower than $k_p\phi$, suggest monomolecular reaction to be essential for explaining the termination mechanism in the polymerisation of multifunctional monomer under the experimental conditions used.

Acknowledgments

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