Temperature effects on the kinetics of photoinitiated polymerization of dimethacrylates

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(Received 1 February 1990; accepted 16 March 1990)

The photoinitiated polymerization of three bisphenol-A-based dimethacrylates is studied. The polymerization rate of the dimethacrylate increases with temperature up to 160°C. Above this temperature depropagation starts to dominate the polymerization and the rate approaches zero above 210°C. In the case of the diacrylates three temperature regions are distinguished. Below 90°C the polymerization rate increases with temperature. Between 90 and 145°C chain transfer suppresses the autoacceleration which results in a decreasing polymerization rate with increasing temperature. Above 145°C depropagation causes an additional rate decrease.

(Keywords: photoinitiated polymerization; dimethacrylates; temperature effects; kinetics)

INTRODUCTION

The photoinitiated bulk polymerization of dimethacrylates leads to densely crosslinked networks[1–4]. Typically, the monomer formulation contains several weight percent of a photoinitiator, which initiates the free-radical chain crosslinking polymerization on exposure to ultraviolet or visible light. The kinetics of the chain polymerization are usually described in terms of initiation, propagation and termination. Under steady-state conditions of diluted systems the following equation is valid[5,6]:

$$R_p = k_p[M]\{\Phi I_0(1 - 10^{-\varepsilon[In]d})/k_t\}^{1/2} \qquad (1)$$

in which R_p is the rate of polymerization, k_p and k_t are the rate constants of propagation and termination, $[M]$ is the monomer concentration, Φ is the overall quantum efficiency for dissociation and initiation, ε is the molar extinction coefficient of the photoinitiator, $[In]$ is the concentration of the photoinitiator, I_0 is the intensity of the incident light, and d is the thickness of the sample.

For chain crosslinking polymerization of dimethacrylates the practical importance of equation (1) is limited. Many sources of deviations are described in the literature. For example, even at a low conversion the hindered mobility of the reactive chain ends causes autoacceleration (Trommsdorff effect) prohibiting a steady-state with a constant free-radical concentration[6–12]. At a higher conversion, the monomer becomes hindered in its diffusion through the vitrifying medium, which causes a rapid deceleration[2,12,13]. The immobilized pendent double bonds of those monomers which have already reacted at one side exhibit a different, concentration-dependent reactivity than the double bonds of the free monomer molecules[2,14]. The termination process may deviate from recombination or disproportion by the formation of inhomogeneities in the pre-gel stage and trapping of free-radicals in inaccessible positions[13,15–17] and by chain transfer to monomer, polymer or photoinitiator. Time- and thus rate-dependent free-volume effects may play a role in enhancing monomer diffusion at higher R_p (Refs. 2, 15, 16). The dissociation efficiency of the photoinitiator may be affected by its environment and may decrease during the course of the polymerization (cage effect)[6].

As a result of all this, the typical rate *versus* time polymerization curves show a steep increase of the rate at the onset of the reaction, followed by a rapid drop and very low rates at the end of the reaction. The reaction virtually stops between 50 and 100% conversion of the vinyl groups, depending on temperature and the molecular structure of the monomer[13,15,18,19].

One of the advantages of photopolymerization is that it can be carried out at room temperature. Nevertheless, in practice the polymerization reactions are often performed at higher temperatures. This may be due to such trivial causes as heating of the samples by the infra-red part of the lamp emission[20], or by the reaction exotherm of thicker samples[13]. In other cases higher polymerization temperatures are desirable, for instance to enhance the rate near the reaction end or to minimize relaxation and the related property changes of the product[21,22]. High temperatures are even indispensable when use is made of special monomer properties such as liquid crystallinity to produce oriented polymeric networks by photopolymerization in the ordered mesophase[23–25].

The influence of temperature on the photopolymerization of dimethacrylates is well documented in the range from room temperature to 100°C[12,15,19,26]. In general, there is a slight increase of the rate with temperature in the case of low viscous or diluted systems. The photodis-

0032-3861/91/040690-06

sociation reaction is almost temperature independent. The activation energy of the propagation reaction is in the order of 25–30 kJ mol^{-1} and that of the termination reaction 16–22 kJ mol^{-1}, which results in a net activation energy of the total reaction of 14–22 kJ mol^{-1} (ref. 6), provided that a second order termination occurs. In the case of more viscous systems the reduced monomer mobility leads to higher activation energies up to values of about 60 kJ mol^{-1} (ref. 26).

Little is known about the photoinitiated crosslinking at even higher temperatures. This paper describes the chain-crosslinking photopolymerization of dimethacrylates up to temperatures of 200°C. A quantitative kinetic analysis has not been aspired to, because in that case many non-trivial problems have to be considered, including thermal initiation, thermal degradation of monomer, polymer and photoinitiator and evaporation of monomer and photoinitiator. Our aim is to provide qualitative insight into the processes dominating high temperature photopolymerization and to provide comparative matter for the photopolymerization of special monomers, such as liquid crystalline diacrylates[23,27].

EXPERIMENTAL

Materials

Figure 1 shows the chemical formulas of the monomers studied. Monomers **1** (Sartomer, West Chester, PA, USA), **2** (UCB, Drogenbos, Belgium) and **3** (AKZO, Amersfoort, The Netherlands) were used without further purification. The content of methacrylate double bonds was determined by thiol addition. Some deviation of the theoretical values was determined by n.m.r. analysis and thought to be caused by multiplication of the alkylene spacer between the acrylate and the aromatic moiety. The photoinitiator α,α-dimethoxydeoxybenzoin (Ciba Geigy, Basle, Switzerland) was dissolved in the monomers under stirring at 80°C.

Techniques

Photopolymerization was studied with a Perkin Elmer DSC-2C modified for u.v. irradiation[15]. Both the reference compartment with empty sample pan and the sample holder containing 0.90 mg of monomer (film thickness = 40 μm) were irradiated with a 4 W fluorescent lamp (Philips TL08, length 20 cm). The lamp emits at 350 nm with a bandwidth of 45 nm at half intensity. The intensity at the sample position is 0.2 mW cm^{-2}. To remove dissolved oxygen, the samples were flushed with nitrogen ($\leqslant$2 ppm oxygen) in the d.s.c. at 25°C for 20 min. Then, in order to keep the high temperature exposure as short as possible, the samples were heated to their polymerization temperature at 160 K min^{-1} and irradiated within 1 min as soon as the baseline had stabilized. The low temperature experiments were carried out after a short thermal exposure at 120°C to allow sufficient flow in the d.s.c. pan in order to achieve a uniform film thickness. R_p is calculated from the reaction exotherm, taking the heat of polymerization of acrylates to be 78 kJ mol^{-1} and that of methacrylates to be 56 kJ mol^{-1} (ref. 6). The conversion is obtained from the integral of the polymerization curves. Dynamic mechanical thermal analysis (d.m.t.a.) of the polymers was performed with a Polymer Labs instrument at a frequency of 1 Hz and a heating rate of 5 K min^{-1}. The T_g values presented are the maxima of the loss tangents, measured on films photopolymerized at 100°C. Viscosity of the monomers was measured with a Contraves RM135 instrument with a cylindrical measuring cup at shear rates between 0 and 500 s^{-1} and temperatures between 25 and 90°C.

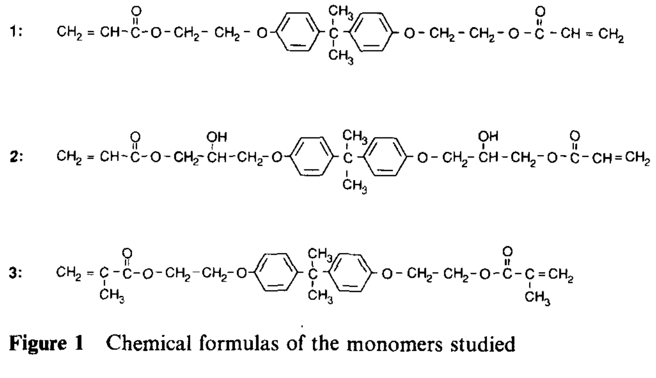

Figure 1 Chemical formulas of the monomers studied

Table 1 Some properties of the monomers and their polymers

Monomer	$[M]$ (mol l^{-1})	η^{25} (Pa s)	E_η (kJ mol^{-1})	T_g (°C)
1	4.82	0.99	63	73
2	4.91	818	129	85
3	4.36	1.50	71	118

RESULTS AND DISCUSSION

Polymerization conditions

Figure 1 shows the dimethacrylates studied. As the kinetics of bulk photopolymerization is known to depend on concentration and molecular mobility, some relevant properties are presented in *Table 1*. Compound **1** is a low viscous diacrylate selected for its low volatility at high temperatures. The hydroxy group of diacrylate **2** leads to a much higher viscosity η and a stronger temperature dependence of η represented by the activation energy E_η. Compound **3** corresponds to **1** but has methacrylate reactive groups.

The initial concentration of double bonds $[M]_i$ has been determined by titration and is in reasonable accordance with theoretical data. The glass transition temperature T_g of the polymer networks is between 70 and 120°C. The transitions occur over a broad temperature range of several tens of degrees and local vitrification may persist up to 130°C for the acrylates and 170°C for the methacrylates.

Photocalorimetric experiments

Figure 2 shows the relationship between the polymerization rate R_p, time and temperature for the three monomers as obtained from isothermal photopolymerization experiments in the d.s.c. At moderate temperatures, the autoacceleration sets in directly from the onset of the u.v. exposure and the maximum rate R_p^{max} is reached within 7 s in the case of the acrylates and within 10 s in the case of the methacrylate. In each case the maximum is followed by a rapid deceleration, after which the reaction proceeds at a rate which is only a small fraction of R_p^{max}.

R_p^{max} of **1** and **2** differ by more than a factor 2 at equal temperatures. The hydrogen bonding in **2** decreases its

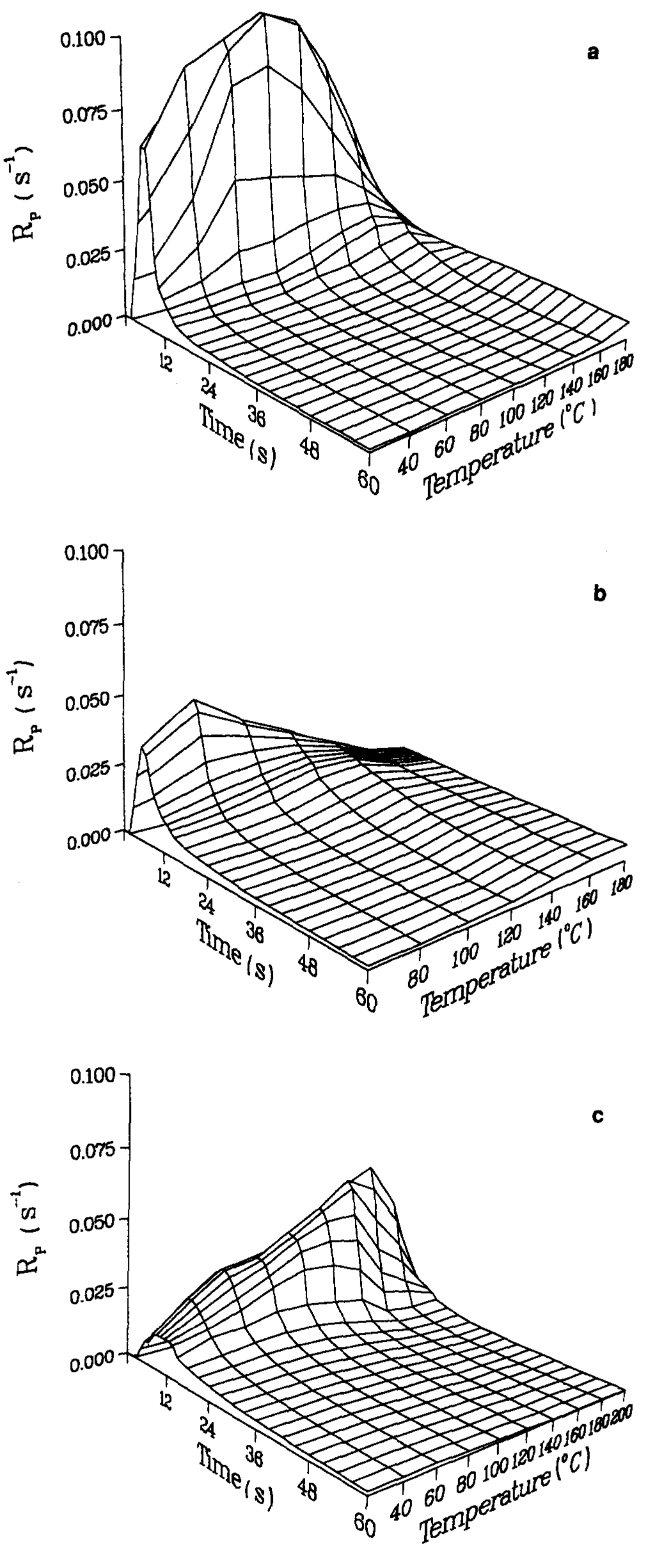

Figure 2 Polymerization rate in moles C=C bonds converted per second, normalized to the initial C=C bonds concentration, as a function of time and temperature of (a) diacrylate **1**, (b) diacrylate **2** and (c) dimethacrylate **3**

diffusional monomer mobility (viscosity effect) and thus the reactivity. The rate difference between **1** and **3** can be explained by the known differences in k_p and k_t between acrylates and methacrylates[6,27].

With respect to the temperature dependence of R_p, it can be seen from *Figure 2* that R_p^{max} goes through a maximum with a decrease at higher temperatures. The maximum polymerization rate for the acrylates is observed at about 80°C and for the methacrylate at 160°C. Of course, various trivial causes for the decrease in R_p^{max} with temperature can be put forward, such as the evaporation of monomer or photoinitiator, thermally initiated dark reaction, thermal degradation of the photoinitiator, etc. Although all these phenomena play a role at the highest temperatures, it was found that their contribution is relatively small on the time scale of our experiments. For instance, postponing the u.v. exposure with a time representing a current polymerization run, while the sample is heated at the polymerization temperature, did not drop the rate more than 10%, depending on the temperature.

The experiments presented in *Figure 2* were carried out with a photoinitiator concentration of 1 wt%. The same tendency was found for other concentrations up to 4.45 wt%. In that case the polymerization rate was higher, obeying the order of 0.5 in $[In]$ at R_p^{max}, but the effect of the temperature was the same. The accuracy of the measurement decreases at higher concentrations due to an overlap of the time to reach R_p^{max} and the response time of the d.s.c. apparatus.

As is stated in the introduction, the shape of the rate *versus* time curves is affected by many variables. The decreasing rate beyond R_p^{max} is caused by monomer depletion and a reduced monomer mobility. Moreover, at polymerization temperatures below T_g, an additional decrease of the rate is expected when the sample vitrifies during the polymerization reaction. The latter may already occur locally at relatively low conversion due to an inhomogeneous polymerization. *Figure 3* shows the conversion at R_p^{max}, χ, as a function of polymerization temperature, illustrating a considerable influence of temperature and monomer type. Because a steady state can be formed almost instantaneously upon irradiation, R_p^{max} should be expected at low conversions. However, the occurrence of autoacceleration in bulk polymerization implies that R_p^{max} is reached at higher conversions. Consequently, χ is determined by the dependence of the autoacceleration on temperature and monomer type, which will be discussed below.

Activation energies

Figure 4 shows an Arrhenius plot of R_p^{max} for the three monomers. *Table 2* summarizes the apparent overall activation energy E_p deduced from the derivatives of these curves. As R_p^{max} occurs at a relatively low and variable conversion (*Figure 3*), activation energies were also calculated from the Arrhenius plots at 30 and 40% conversion of the double bonds. From *Figure 4* three temperature regions can be distinguished.

In the low temperature (LT) region below 70–90°C, R_p^{max} increases with temperature. E_p^{max} is about 10 kJ mol^{-1} for the low-viscous monomers **1** and **3** and much higher and not constant for the highly viscous monomer **2**. E_p increases with conversion, as already described in literature for hexanediol diacrylate[12].

In the medium temperature (MT) region, which lies roughly between 90 and 145°C, R_p^{max} decreases with temperature for the two diacrylates. Correspondingly, negative E_p^{max} values are found. At higher conversions, where the autoacceleration is less predominant due to a hindered monomer diffusion, $E_{\rm pol}$ remains negative for **1**, but becomes positive again for **2**. The methacrylate **3** shows the normal behaviour, as in the LT region.

In the high temperature (HT) region above about

Table 2 Apparent overall activation energy (kJ mol^{-1}) of photopolymerization in the distinguishable temperature regions at R_p^{max} and at 30 and 40% conversion

	LT region			MT region			HT region		
Monomer	R_p^{max}	30%	40%	R_p^{max}	30%	40%	R_p^{max}	30%	40%
1	10	14	30[a]	−16	−22	−22	−57	−64	−59
2	40−116[a]	−[a]	−[a]	−21	0	22	−52	−62	−54
3	10	29	33	10	29	33	−100[a]	−130[a]	−160[a]

[a] In this temperature region no linear Arrhenius plot was obtained; indicated data are estimations and depend largely on the temperature limits

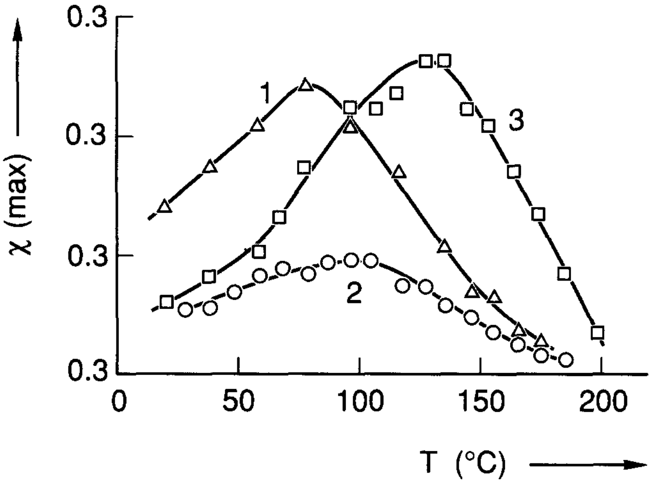

Figure 3 Conversion χ at R_p^{max} as a function of the polymerization temperature. The numbers in the figure correspond to the monomers presented in *Figure 1*

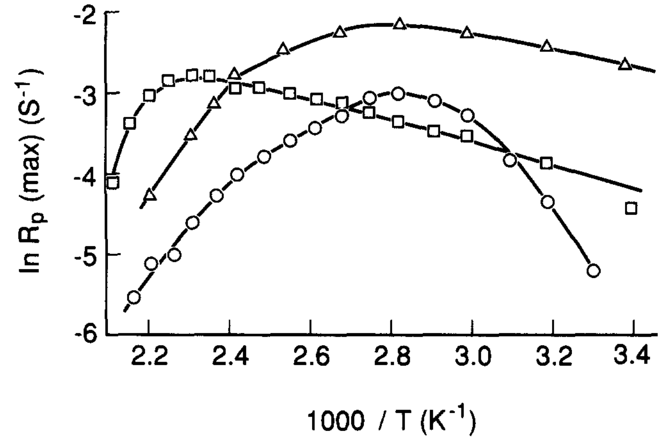

Figure 4 Arrhenius plots of R_p^{max} of the diacrylates **1** (△) and **2** (○) and the methacrylate **3** (□)

145°C, there is a transition in the Arrhenius plots of the two acrylates, showing a faster decrease of R_p^{max} with increasing temperature. E_p becomes highly negative with values of about $-60\,kJ\,mol^{-1}$. In the case of the dimethacrylate, R_p^{max} starts to decrease above 160°C with $E_p \leqslant -100\,kJ\,mol^{-1}$.

Photopolymerization in the HT region

The highest temperature region, above 145°C for **1** and **2** and 160°C for **3**, is characterized by a decreasing polymerization rate and end conversions with increasing temperature. Above 210°C the rate approaches zero and polymerization seems to be close to its ceiling temperature. Although this is the case for both the diacrylates and the dimethacrylate, the shapes of the polymerization curves differ considerably at these high temperatures, as is demonstrated in *Figure 5*. At 180°C the rate curve of **3** is still dominated by the autoacceleration peak at the reaction onset, whereas **1** and **2** form an apparent steady state during which R_p decreases gradually with time. For monomer **2**, a plot of R_p *versus* the remaining double bond concentration results in a linear curve over a broad concentration range, as shown in *Figure 6* for different temperatures in the relevant range. Assuming that there is no topological hindrance at such low conversions, extrapolation to $R_p = 0$ should yield the equilibrium monomer concentration $[M]_{eq}$ related to the reaction temperature T by

$$\ln[M]_{eq} = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \qquad (2)$$

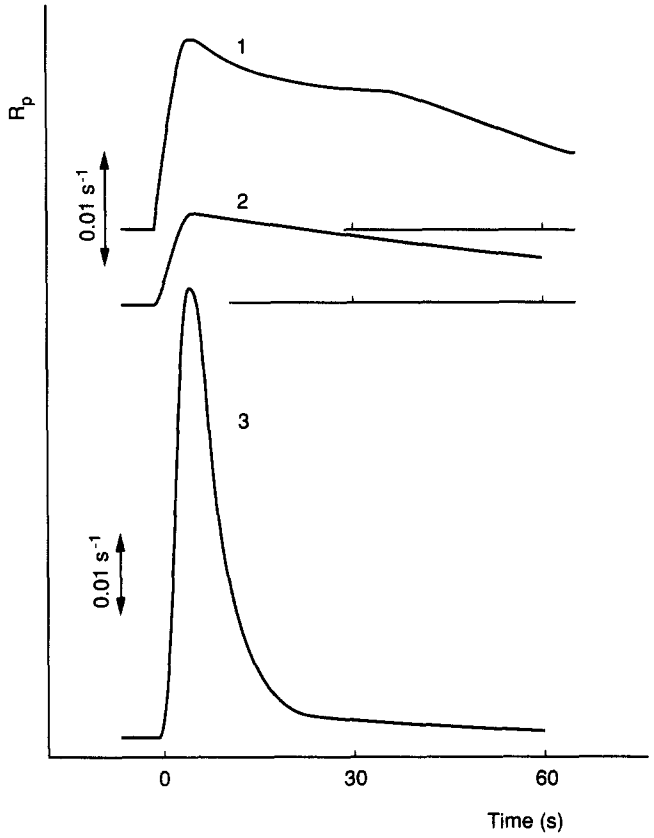

Figure 5 Isothermal d.s.c. traces of the photopolymerization of the diacrylates **1** and **2** and the dimethacrylate **3** at 180°C

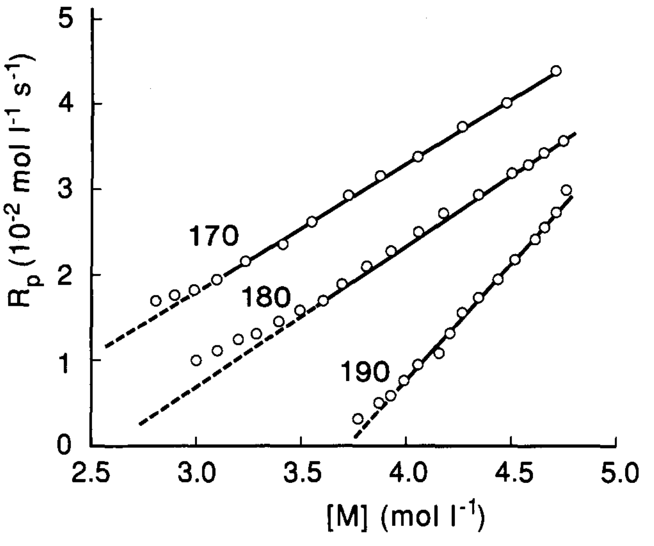

Figure 6 Polymerization rate of diacrylate **2** as a function of the monomer concentration during the course of the photopolymerization at the indicated temperatures (°C)

The reaction enthalpy ΔH^0 and entropy ΔS^0 refer to the pure monomer as the standard state; R is the gas constant. A rough estimation of the thermodynamic reaction parameters by plotting $\ln[M]_{eq}$ *versus* $1/T$ through the three data points obtained from *Figure 5* yielded $\Delta H^0 = -70$ kJ mol^{-1}, $\Delta S^0 = -149$ kJ mol^{-1} K^{-1} and $T_0 = 475$ K for the bulk monomer. In literature the ΔH^0 for methyl acrylate is given as -78 kJ mol^{-1}. ΔS^0 and T_c are unknown. From this result it was concluded that also in the case of diacrylates the propagation–depropagation equilibrium determines the polymerization rate and the conversion at these high temperatures. For the two other monomers comparable plots were not made due to the lack of linearity of R_p *versus* $[M]$, caused by autoacceleration. Estimation of $[M]_{eq}$ from the end-conversion by integration of the rate *versus* time curves is very inaccurate because of the asymptotic approach to zero R_p, the corresponding base-line deviations of the d.s.c. at these high temperatures and the occurrence of side and degradation reactions at longer exposure times. After prolonged irradiation above 220°C the diacrylates remained liquid-like when checked at these high temperatures. Cooling to room temperature gave yet some polymerization due to the presence of free-radicals and a shift of the propagation–depropagation equilibrium.

Photopolymerization in the MT region

As could be seen from *Figure 4*, both diacrylates **1** and **2** have a characteristic temperature region in between the ones which are dominated by propagation (<90°C) and depropagation (>145°C), respectively. In this temperature region it is mainly the autoacceleration which diminishes with increasing temperature (*Figures 2a* and *b*), pointing to the fact that termination of the chain reaction becomes more prominent. This could be caused by a mobilization of the free radical chain ends in the gel stage of the reaction at these high temperatures. However, a similar effect was not observed during the polymerization of the methacrylate monomer **3**. Therefore, it is more likely that the termination is enhanced by chain transfer of the free-radicals of poly(**1**) and poly(**2**), which increases with temperature. Transport of remobilized free radicals might then result in an increase of the recombination reaction or in an increase of trapped radicals which are positioned on sites which are inaccessible to monomer diffusion. The idea that in the MT region chain transfer starts dominating the rate of polymerization is supported by the following observations.

Because the methacrylate is insensitive to the retardation in the MT region, the α-H of the vinyl group is likely to play a vital role in the mechanism of radical hopping. Kloosterboer *et al.*[28] have already shown by studying partly deuterated samples that chain transfer through α-H abstraction provides an important route for termination.

The activation energies for chain transfer of a growing acrylate polymer to its monomer, as can be deduced from an Arrhenius plot of data presented in the literature[29], are higher than those of the propagation reaction, pointing to an increasing importance of chain transfer at higher temperatures. In the case of PMMA the activation energies of propagation and chain transfer are of the same order.

The hydroxy group in **2** is known[30] to enhance chain transfer, which explains that the suppression of the autoacceleration is even more pronounced for this compound.

Free-radical transfer may proceed until the radical is trapped or recombined. E.s.r. measurements[31] showed the existence of long lived trapped free radicals. Best *et al.*[17] showed that trapped radicals are positioned in mid-chain segments of the networks which had the highest strained conformation. This position can only be obtained after chain transfer. However, free-radical trapping plays a limited role, because the main termination mechanism at 100°C is based on a bimolecular reaction, as is concluded from the apparent order of 0.5 in $[In]$. Polymerization at 150°C revealed the same order, showing that the mechanism of termination is not subjected to major changes in the MT region.

CONCLUSIONS

The rate of photopolymerization of a dimethacrylate decreases at temperatures above 160°C. Above this temperature the depropagation reaction becomes important, ultimately resulting in a zero rate. In the case of the photopolymerization of diacrylates the polymerization rate decreases already above 90°C. It is suggested that above this temperature termination through chain transfer suppresses the autoacceleration. Above 145°C the depropagation reaction dominates the photopolymerization.

ACKNOWLEDGEMENT

The helpful discussions with Dr J. G. Kloosterboer and the support with the data assimilation from Dr I. Heynderickx are gratefully acknowledged.

REFERENCES

1 Kloosterboer, J. G. *Adv. Polym. Sci.* 1988, **84**, 1

2 Kloosterboer, J. G., Lijten, C. F. C. M. and Boots, H. M. J. *Makromol. Chem., Macromol. Symp.* 1989, **24**, 223

3 Roffey, C. G. 'Photopolymerization of Surface Coatings' Wiley-Interscience, Chichester, 1982

4 Green, G. E., Stark, B. P. and Zahir, S. A. *J. Macro. Sci.-Revs. Macro. Chem.* 1981, **C21**, 187

5 Joshi, M. *J. Appl. Polym. Sci.* 1981, **26**, 3945

6 Odian, G. 'Principles of Polymerization', 2nd edn. Wiley-Interscience, New York, 1981

7 Tulig, T. J. and Tirrell, M. *Macromolecules* 1981, **14**, 1501

8 Ito, K. *Polymer J.* 1980, **12**, 499

9 Burnett, G. M. and Duncan, G. L. *Makromol. Chem.* 1961, **51**, 177

10 Mangaraj, D. and Patra, S. K. *Makromol. Chem.* 1967, **104**, 125

11 Vollmert, B. 'Polymer Chemistry', Springer, Berlin, 1973, pp. 45, 68

12 Tryson, G. R. and Schultz, A. R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 2059

13 Kloosterboer, J. G. and Lijten, G. F. C. M. *Polymer* 1987, **28**, 1149

14 Malinsky, J., Klaban, J. and Dusek, K. J. *J. Macromol. Sci. Chem.* 1971, **A5**, 1071

15 Kloosterboer, J. G., van de Hei, G. M. M., Gossink, R. G. and Dortant, G. C. M. *Polym. Commun.* 1984, **25**, 322

16 Hoyle, C. E., Hensel, R. D. and Grubb, M. B. *Polym. Photochem.* 1984, **4**, 69

17 Best, M. E. and Kasai, P. H. *Macromolecules* 1989, **22**, 2622

18 Orier, B., Wilkes, G. L. and Ganesh Kumar, N. *Polym. Prepr.* 1985, **26**, 281

19 Moore, J. E. 'UV Curing: Science and Technology' (Ed. S. P. Pappas), Technology Market Publishers, Stamford (CT), 1978, Ch. 5

20 Bouten, P. C. P., Broer, D. J., Jochem, C. M. G. and Meeuwsen, T. P. M. *Polym. Eng. Sci.* 1989, **29**, 1172

21 Gossink, R. G. *Angew. Makromol. Chem.* 1986, **145/146**, 365

22 Zwiers, R. J. M. and Dortant, G. C. M. *Appl. Optics* 1985, **24**, 4483

23 Broer, D. J., Boven, J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1989, **190**, 2225

24 Broer, D. J., Hikmet, R. A. M. and Challa, G. *Makromol. Chem.* 1989, **190**, 3201

25 Broer, D. J. and Heynderickx, I. *Macromolecules* 1990, **23**, 2474

26 Doornkamp, A. T. and Tan, Y. Y. *Polym. Commun.* 1990, **31**, 3

27 Broer, D. J., Mol, G. N. and Challa, G. in press

28 Kloosterboer, J. G. and Lijten, G. F. C. M. *Polym. Commun.* 1987, **28**, 2

29 Eastmond, C. G. 'Comprehensive Chemical Kinetics, Free Radical Polymerization' (Eds C. H. Bamford and C. F. H. Tipper) Elsevier, Amsterdam, 1976, Ch. 3

30 Dowbenko, R., Friedlander, C., Gruber, G., Prucnal, P. and Wismer, M. *Progr. Org. Coat.* 1983, **11**, 71

31 Kloosterboer, J. G., Van de Hei, G. M. M. and Lijten, G. F. C. M. 'Integration of Fundamental Polymer Science and Technology' (Eds L. A. Kleintjes and P. Lemstra) Elsevier Applied Science, London, 1986, p. 198