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Kinetic study of the photoinitiated polymerization of a liquid crystalline diacrylate monomer by d.s.c. in the isothermal mode

A. T. Doornkamp, G. O. R. Alberda van Ekenstein and Y. Y. Tan*
Department of Polymer Chemistry, State University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
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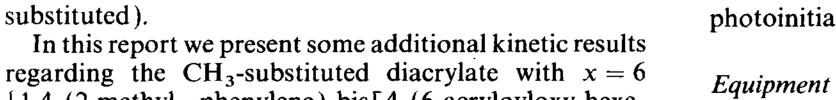
The photoinitiated polymerization of the liquid crystalline (LC) diacrylate monomer 1,4-(-2-methyl phenylene)-bis[4-(6-acryloyloxy-hexamethyleneoxy)benzoate] with $T_{k,n} = 85°C$ and $T_i = 118°C$, was studied by d.s.c. at various temperatures under different conditions. In the crystalline state there is a low polymerization rate which increases on approaching $T_{k,n}$. In the LC state the initial rate is temperature independent up to 10–20°C above T_i signifying that a better monomer ordering in the LC state does not appear to affect the rate. Rate invariance on elevation of temperature may be the consequence of a compensation of propagation rate increase by termination rate increase. At still higher temperatures the rate drops probably due to depropagation. The 0.65 order in photoinitiator (= 2,2-dimethoxy-2-phenylacetophenone) points to the presence of a first-order termination mode besides the usual second-order mode. The results on temperature dependence were compared with those of a LC monoacrylate monomer, 4-acryloyloxyhexamethyleneoxybenzoic acid.

(Keywords: kinetics; photoinitiated polymerization; d.s.c.)

INTRODUCTION

Following an investigation on the photoinitiated polymerization of a polyesterurethane diacrylate[1], a liquid crystalline (LC) diacrylate was studied along the same lines employing d.s.c. Such monomers are interesting in view of the possibility of studying polymerization kinetics in the mesomorphic phase (in the unoriented and oriented state) besides the solid and isotropic phases. The syntheses of LC diacrylates and dimethacrylates have been described earlier[2–4] and only recently has their photoinitiated polymerization resulting in densely crosslinked films been examined by Broer *et al.*[5–7]. These authors investigated several members of the homologous series of 1,4-phenylene (and the monomethyl-substituted 1,4-phenylene)-bis[4-(x-acryloyloxy-alkyloxy) benzoate]:



with $x = 4$–11 (unsubstituted) and $x = 4$–6 (CH_3-substituted).

In this report we present some additional kinetic results regarding the CH_3-substituted diacrylate with $x = 6$ {1,4-(2-methyl phenylene)-bis[4-(6-acryloyloxy-hexamethyleneoxy)benzoate], for short diacrylate monomer **1**} because of its attractive low transition temperatures of $T_{k,n} = 85°C$ and $T_i = 118°C$ which are practically identical with values reported previously[7].

EXPERIMENTAL

Materials

The diacrylate monomer **1** was synthesized at Philips Research Laboratories, Eindhoven, The Netherlands, according to a procedure described elsewhere[5]. The monoacrylate monomer 4-acryloyloxyhexamethyleneoxybenzoic acid (monomer **2**) was obtained from UCB, Drogenbos, Belgium. It was recrystallized from 2-propanol with $T_{k,n} = 85°C$ and $T_i = 106°C$. 2,2-Dimethoxy-2-phenylacetophenone (alternatively named benzyldimethylketal or α,α-dimethoxydeoxybenzoin; tradename Irgacure 651 of Ciba-Geigy, Basle, Switzerland) was used as the photoinitiator (white powder, m.p. = 63°C).

Equipment

An adapted Perkin Elmer DSC-2 instrument was used to measure the rates of polymerization induced by u.v. irradiation. The intensity of the radiation in the region of 320–380 nm was measured with the aid of a

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*To whom correspondence should be addressed

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Spectroline radiometer to be 0.12 mW cm^{-2}. Further details are given elsewhere[1].

Polymerization

Samples were prepared by mixing the monomer with the desired amount of initiator in dichloromethane. After dissolution in and evaporation of the solvent a homogeneous powdery crystalline product was obtained. A standard d.s.c. aluminium cup was filled (0.5–1 mg), and after flushing the d.s.c. apparatus for 15 min with N_2 and raising the temperature to the desired polymerization temperature (T_{pol}), the shutter of the u.v. lamp was opened. For further details, see reference 1.

In order to examine the polymerization of oriented **1**, cups with an alignment coating[8] were used. For this purpose, polyimide (Pyralin 2566, Du Pont) as alignment substrate and thinner (T 3095, Du Pont) was applied as a very thin layer on Al foil by means of a Convac ST 143 spin coater. To secure good adhesion to the Al foil a coupling agent, γ-aminopropyltriethoxysilane, was used. The thickness of the layers was ~3–5 μm according to calibration curves for different spincoater speeds. Orientation of the layer was achieved by rubbing it in one direction with a velvet cloth. From such Al foils, rubbed and unrubbed, d.s.c. cups were made. In contact with a rubbed surface, the LC monomer is homogeneously oriented[9].

Data analysis of isothermal d.s.c. curves

Conversion–time curves were obtained according to a previously described procedure[1]. Initial polymerization rates, $v_{p,o}$, were calculated from the initial slopes of these curves. To calculate polymerization rates at the maximum of the d.s.c. curves, $v_{p,max}$ (wt% conversion s^{-1}), the following formula was used:

$$v_{p,max} = \frac{h_{max} \times 4.18 \times 10^{-3} \times M}{w \times 25 \times \Delta H_{p,o}} \times 100$$
$$(\text{mol\% C=C s}^{-1})$$

where h_{max} is the maximum height of the d.s.c. curve (cm), w is the sample weight (g), M is the molar mass of diacrylate **1** (672 g mol^{-1}) and $\Delta H_{p,o}$ is the polymerization enthalpy (156 kJ mol^{-1}). The number 25 is related to the full scale of 25 cm of recorder paper which corresponds to 1 mcal s^{-1} and 4.18×10^{-3} is a conversion factor (mcal to J).

RESULTS AND DISCUSSION

Influence of temperature on the polymerization rate

The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, which has found widespread applications in u.v. curing[10], produces free radicals upon photolysis. Therefore it may be said that propagation proceeds according to a radical mechanism[11–13].

The photopolymerization of **1** was performed in three distinct temperature regions: (A) at $T_{pol} < 85°C$ where the sample was a crystalline powder; (B) at $85°C < T_{pol} < 118°C$ where the sample was in the LC phase; (C) at $T_{pol} > 118°C$ where the sample was in the isotropic phase.

The results are shown in *Figure 1* where the initial polymerization rates, ln $v_{p,o}$ (mol l^{-1} s^{-1}), are plotted *versus* the reaction temperature (in °C), for systems containing different initiator concentrations of 0.48, 0.68, 2.23 and 4.5 wt%, respectively. It should be noticed that the presence of initiator depresses the transition temperatures[5,9], especially T_i, e.g. with 0.68 wt% of initiator $T_{k,n}$ decreased from 85.0 to only 84.3°C whereas T_i dropped 3°C from 118 to 115°C.

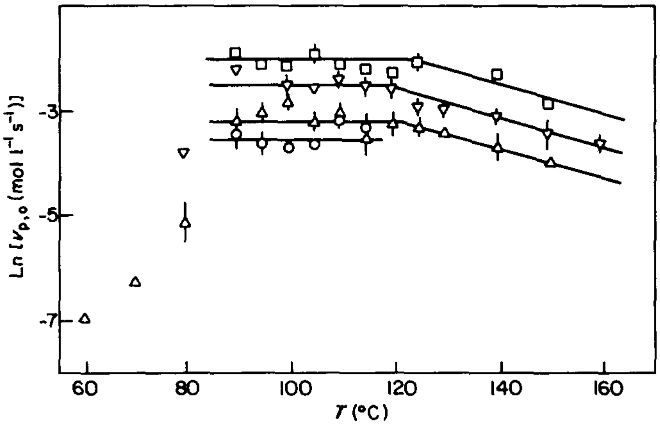

Figure 1 Initial polymerization rates *versus* temperature of diacrylate **1** with different initiator (Irgacure 651) concentrations: (○) 0.48; (△) 0.68; (▽) 2.2; (□) 4.5 wt%. Incident light intensity = 0.12 mW cm^{-2}

In interval A, polymerization with 0.68 wt% initiator was (very) low, but increased from 60 to 80°C (maximum conversion ~30%). This is understandable because of the highly reduced mobility of the molecules in the crystal lattice. Nevertheless it is still remarkable that some reaction did occur signifying that the double bonds should be within a proper distance with respect to one another. The crystals of the monomer were too small however to render a determination of the crystal lattice by X-ray diffraction feasible.

In interval B initial rates were obviously much more rapid that in A. They increased with initiator concentration, and appeared to be essentially unaffected by the temperature. This temperature independence of $v_{p,o}$ even extended beyond the T_i (see also later). Previously[1] such behaviour was also found, though with a non-LC diacrylate. This could be rationalized by a compensation of the rate increase of the propagation step by the rate increase of the termination step with rising temperature. This explanation may also apply to the present system. Therefore one must conclude that the polymerization behaviour in the nematic phase is not different from that in the isotropic phase. This implies that, although the monomer molecules are aligned in the nematic phase, the degree of arrangement of double bonds with respect to one another is not enough to affect the diffusion rates of monomer and chain radicals as compared to its random orientation in the isotropic phase. This might be different in the smectic phase where the double bonds are much better arranged with respect to each other.

This temperature invariance may be accidental, however, e.g. a slow decrease in rate in the nematic mesophase was observed on polymerizing monomer **2**.

In interval C monomer **1** showed a decrease of $v_{p,o}$ only after ~10–20°C beyond T_i, in contrast to monomer **2** where $v_{p,o}$ dropped rapidly immediately after reaching T_i at 106°C (cf. *Figures 1* and *2*). Several explanations can be proposed for these decreases of the rate with temperature elevation. The obvious one is increasing evaporation of the initiator as could be established by

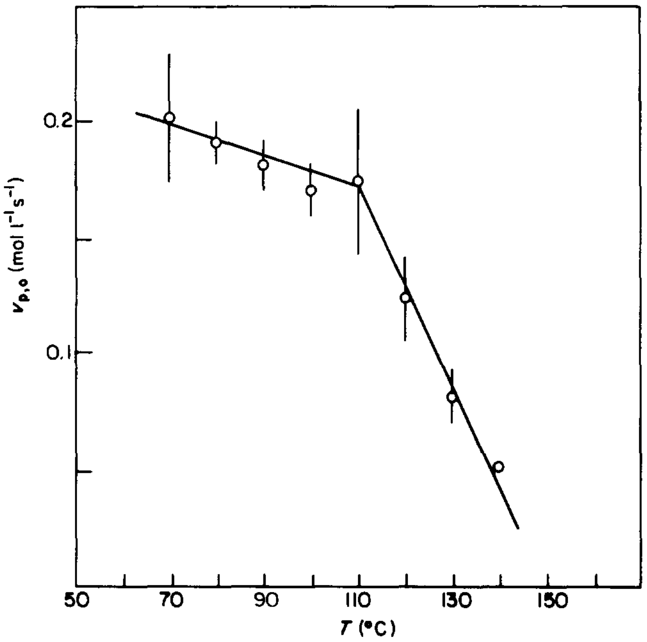

Figure 2 Initial polymerization rates *versus* temperature of acrylate 2. Initiator concentration = 1.31 wt%. Incident light intensity = 0.12 mW cm^{-2}. Pre-isotropization temperature = 120°C

Table 1 Initial polymerization rate at 100°C after pre-isotropization at 140°C

Pre-isotropization time (min)	$v_{p,o}$ (mol l^{-1} s^{-1})
0	0.0517
20 s	0.0553
1	0.0577
2.5	0.0510
5	0.0428
10	0.0302

Initiator concentration = 0.70 wt%

blank experiments whereby sole initiator present in the d.s.c. cup disappeared rapidly, as well as by polymerizations whereby the use of a lower melting (more volatile) photoinitiator led to reduced rates. However, this explanation could be rejected by the following experiments.

Samples of **1**, containing 0.70 wt% of Irgacure 651, were 'annealed' for various periods at 140°C and then polymerized at 100°C. The rate started to decrease only after annealing for 3 min (*Table 1*), which signifies that the rate at 140°C was affected by initiator evaporation only when samples were kept at this temperature for > ~3 min before exposure at 100°C. Since the annealing was done generally within 2 min, evaporation of initiator could not be the (principal) cause for the drop in rate beyond T_i.

Therefore it is more likely that the rate decrease is due to the increasing competition of the depropagation step. According to Broer[14], a non-volatile polymeric photoinitiator also showed a decrease in rate above T_i, supporting this hypothesis. It could be that depropagation is more or less suppressed by the mesophase in the case of monomer **2**. It should be remarked that depropagation may be accompanied by a decreasing gel (Trommsdorff) effect giving rise to enhanced termination[5].

Influence of sample pre-isotropization on the polymerization rate

In the above experiments, T_{pol} was attained directly from room temperature. It is known that the nematic state of diacrylate **1** displays a large undercooling[6] down to 25°C. Accordingly, in the following set of experiments with 0.68 wt% initiator T_{pol} was attained from the isotropic phase. Thus the samples in the d.s.c. apparatus were first 'annealed' at 130°C for ~2 min ('pre-isotropization'), and then cooled rapidly to T_{pol}. The results are shown in *Figure 3* (▲) together with the comparable results from *Figure 1* (△). Owing to the scatter of experimental points, no significant influence of T_{pol} on $v_{p,o}$ could be deduced for polymerizations down to 85°C with respect to the way in which T_{pol} was reached, and the constant initial rate level was maintained even down to 60°C as long as the undercooled LC phase was present. Hence, the nature of the phase of the sample determines the magnitude of the initial polymerization rate rather than the reaction temperature.

Influence of monomer orientation on the polymerization rate

Orientation of diacrylate **1** was realized by using an orientating substrate as described in the Experimental section. The measurements were carried out with samples containing 0.68 wt% initiator in the temperature range 85–120°C. Although a slight tendency of rate increase is evident in *Figure 3* (▽), the effect is too small for a definitive conclusion. Consequently, homogeneous orientation which may be considered as an improvement of orientation in domains, does not seem to change significantly the initial rate of polymerization.

Maximum polymerization rate as a function of temperature

Instead of $v_{p,o}$ we may also plot $v_{p,max}$, which corresponds to the maximum of the d.s.c. curve, *versus* T_{pol}. If classical kinetics prevail, it may be anticipated that $v_{p,max}$ is identical with $v_{p,o}$ under steady-state conditions[15].

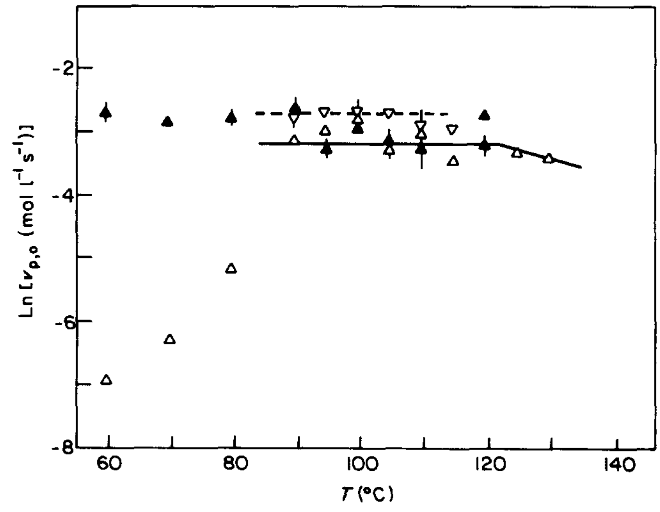

Figure 3 Initial polymerization rates *versus* temperature of diacrylate **1** samples heated directly to T_{pol} (△) [in cups with a rubbed polyimide coating (▽)] or first annealed at 130°C (pre-isotropization) followed by cooling to T_{pol} (▲) before u.v. illumination. Initiator concentration = 0.68 wt%

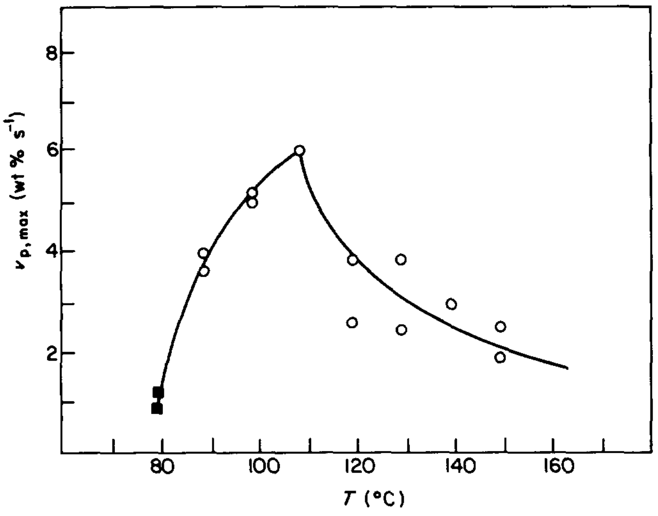

Figure 4 Maximum polymerization rate, $v_{p,max}$, *versus* reaction temperature for the polymerization of diacrylate **1**: (■) polymerization in the crystalline state; (○) polymerization in the LC phase. Initiator concentration = 0.68 wt%. Incident light intensity = 0.12 mW cm^{-2}

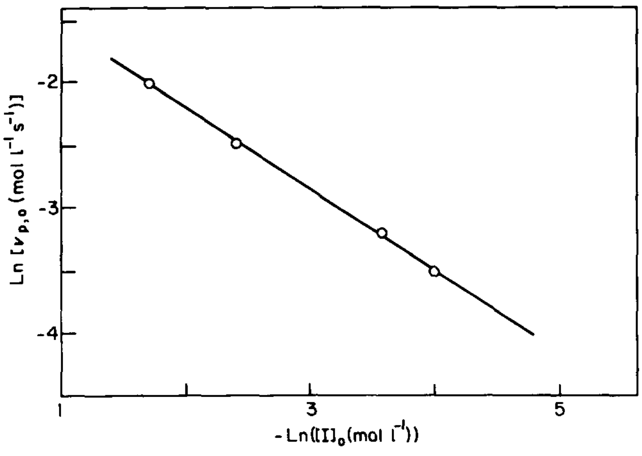

Figure 5 Initial polymerization rate of diacrylate **1** *versus* initial initiator concentration $[I]_o$ in the temperature-independent region (85–120°C)

In *Figure 4* $v_{p,max}$ is plotted as a function of T_{pol} for the system with 0.68 wt% initiator. The $v_{p,max}$ increases with temperature, reaches a maximum around 110°C (383 K) and decreases beyond it. This result is in complete contrast with the temperature independence of $v_{p,o}$ in *Figure 3* because of the non-stationary behaviour of the crosslinking reaction.

The maximum of $v_{p,max}$ near T_i may be due to various reasons. In view of what has been said before, the most likely explanation would be the influence of the depropagation reaction. It may be that this reaction is suppressed in the mesomorphic phase. It has also been suggested that a possible chain transfer reaction via the α-H of the acrylate groups[16] is suppressed in the mesomorphic state[7]. Both factors, depropagation and chain transfer, may contribute to a diminished gel effect in the isotropic phase resulting in a lowering of $v_{p,max}$.

'Maximum' conversions

These are conversions when the d.s.c. curves have returned to the baseline which does not mean that the reaction has definitely stopped at this point; it can continue at a rate too slow to be detectable by the apparatus[1,7]. In the LC and amorphous states up to ~130°C, maximum conversions reached 60–~100% with increasing initiator concentration. Above 130°C maximum conversions were somewhat lower. In the crystalline state near $T_{k,n}$ maximum conversions could reach surprisingly high values of 33 and 50% with initiator concentrations of 0.68 and 2.2 wt%, respectively.

Order of initiator concentration

From *Figure 1* one may estimate the order of initiator concentration $[I]_o$, in the temperature interval B. In *Figure 5* the gross average rates are given in this interval, i.e. in the LC region (taken from *Figure 1*), as a function of $[I]_o$. An order of $[I]_o$ of ~0.65 is obtained, indicating the presence of a first-order termination reaction besides the normal second-order termination reaction. This was also found previously with a non-LC diacrylate[1] and even for a monoacrylate in the nematic phase[17]. First-order termination can be related to trapping of radicals which can occur at the beginning of the crosslinking reaction[16]. These long-life radicals cause the continuing slow reaction after the end of the experiments.

CONCLUSIONS

It appears that in the crystalline state the molecules of diacrylate monomer **1** are arranged in such a way that polymerization is possible. With regard to the melt it seems that the LC state does not strongly affect the initial polymerization rate. The latter seems also to be relatively unaffected by additional alignment of the monomer molecules in the LC state. The temperature independence of the initial rate in the LC and the amorphous regions may be a consequence of a balance between propagation and termination steps. The decrease in initial rate at high temperatures may be due to the occurrence of the depropagation reaction. First-order termination, possibly mainly due to trapping of radicals, takes place besides bimolecular termination.

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REFERENCES

1 Doornkamp, A. and Tan, Y. Y. *Polym. Commun.* 1990, **31**, 362
2 Strzelecki, L. and Liebert, I. *Bull. Soc. Chim. France* 1973, 605
3 Arslanov, V. V. and Nikolajeva, V. I. *Vysokomol. Soedin. Ser. B* 1984, **26**, 208
4 Galli, G., Laus, M. and Angeloni, A. S. *Makromol. Chem.* 1986, **187**, 289
5 Broer, D. J., Boven, J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1989, **190**, 2255
6 Broer, D. J., Hikmet, R. A. M. and Challa, G. *Makromol. Chem.* 1989, **190**, 3201
7 Broer, D. J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1991, **192**, 59

8 Haase, W. in 'Side Chain Liquid Crystalline Polymers' (Ed. C. B. McArdle), Blackie, Glasgow, 1989, p. 315

9 Broer, D. J., Finkelmann, H. and Kondo, K. *Makromol. Chem.* 1988, **189**, 185

10 Decker, C. and Moussa, K. *Makromol. Chem.* 1990, **191**, 963

11 Ledwith, A. *Pure Appl. Chem.* 1977, **49**, 431

12 Groenenboom, G. J., Hageman, H. J., Overeem, T. and Weber, A. J. M. *Makromol. Chem.* 1982, **183**, 281

13 Allen, N. S., Catalina, F., Green, P. N. and Green, W. A. *Eur. Polym. J.* 1986, **22**, 49

14 Broer, D. J. personal communication, 1991

15 Alberda van Ekenstein, G. O. R. and Tan, Y. Y. *Eur. Polym. J.* 1988, **24**, 1073

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

17 Krentsel, B. A. *Midlands Macromol. Monogr.* 1977, **3**, 117