Thermochimica Acta, 205 (1992) 139–144
Elsevier Science Publishers B.V., Amsterdam

Study of the isothermal bulk polymerization of dimethyl phenyl methacrylates by differential scanning calorimetry

Jovanka M. Filipović, Dušanka M. Petrović-Djakov, Ljubica P. Vrhovac and Jovan S. Veličković

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 494, YU-11000 Belgrade (Yugoslavia)

(Received 18 November 1991)

Abstract

The kinetics of the free radical polymerization of six isomeric dimethyl phenyl methacrylates, initiated with dilauroyl peroxide, were examined by DSC in the temperature range 323–398 K. It was found that the rates of polymerization depend on the mode of methyl substitutions in the aromatic ring; differences for the enthalpies of polymerization and Arrhenius activation energies were also observed. The differences in reaction rate constants tend to decrease with increasing polymerization temperatures and by extrapolation to higher temperatures vanish almost completely at about 400 K.

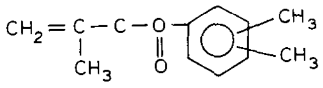
INTRODUCTION

The kinetics of the free radical polymerization of various arylalkyl methacrylates have been studied extensively in this laboratory, using mostly dilatometric and occasionally gravimetric techniques [1–3]. It was established that the overall free radical reaction constants k' depend on the monomer structure, more specifically on the size and position of the alkyl groups substituting the aromatic ring in the monomer lateral substituent. Considerable differences were observed when polymerizing dimethyl phenyl methacrylates in the temperature interval 323–353 K, using dilatometric techniques [3]. The present work is an extension of these investigations to a higher temperature interval, suitable only for differential scanning calorimetry (DSC) measurements, and includes all six possible isomeric dimethyl phenyl methacrylates, i.e. 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethyl phenyl methacrylates (DMPhMA), represented by the general formula shown in Scheme 1.

All six monomers were synthesised according to a procedure described previously for *o*-, *m*- and *p*-tolyl methacrylates [1]. The purity of the

---

Correspondence to: J.S. Veličković, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 494, YU-11000 Belgrade, Yugoslavia.



Scheme 1.

monomers was checked by elemental analysis, GC and IRS. Dilauroyl peroxide initiator (DLP; from Merck) was crystallized twice from methanol and dried at 313 K in vacuo. The initiator concentration in all bulk polymerizations was constant, i.e. 0.5 mol l^{-1}. The DSC measurements were performed with a Perkin–Elmer DSC-2 thermoanalyzer. Polymerizations were first carried out dynamically in order to determine a convenient temperature range for DSC measurements, covering an interval from 323 to 473 K; subsequently the reactions were carried out isothermally at various temperatures within the range 338–393 K. The enthalpies were determined from the area under the DSC curve, obtained after back extrapolation of the straight line recorded after the polymerization was terminated. The calorimeter was calibrated by measuring the heat of fusion of indium. The reproduciblity of the results was satisfactory except at 393 K. The results recorded at 398 K were obtained by extrapolation.

RESULTS AND DISCUSSION

The curves obtained in the course of the isothermal polymerization of 2,5-DMPhMA at several temperatures are presented in Fig. 1. The curves indicate the existence of an initial interval, a steady-state section and an autoacceleration of the reaction at higher temperatures and at higher conversions. Similar results were obtained for all other investigated monomers. Very elongated flat thermograms and those with an initial steep heat evolution were not suitable for rate constant evaluations. Occasionally initial induction periods were observed at lower temperatures, which decreased with increasing temperatures and vanished completely at 363 K.

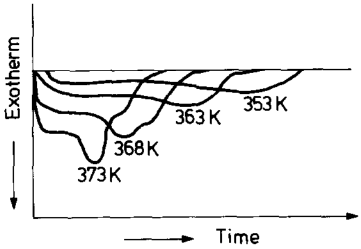


Fig. 1. DSC thermograms of 2,5-dimethyl phenyl methacrylate monomer polymerized at 353, 363, 368 and 373 K.

TABLE 1

Enthalpies of polymerization of dimethyl phenyl methacrylates, corrected for residual monomer content, at various temperatures and mean values obtained

Temp. T (K)	Enthalpy of polymerization, $-\Delta H_p$ (kJ mol^{-1})					
	3,4-	3,5-	2,4-	2,5-	2,3-	2,6-
348	56.6	–	47.7	–	–	–
353	56.2	–	47.3	48.7	–	–
358	57.9	49.7	48.8	52.5	48.2	–
363	59.9	52.4	51.6	52.0	46.2	34.2
368	59.5	54.2	48.8	53.9	49.0	38.2
373	59.1	51.2	48.9	48.7	49.1	38.8
378	58.1	55.8	50.1	49.0	48.1	35.8
383	60.6	53.5	49.1	46.7	–	–
Mean values	58.5	52.8	49.0	50.2	48.1	36.8

The enthalpies $-\Delta H_p$ calculated from the DSC surface and the monomer mass (ranging between 5 and 10 mg) are presented in Table 1. From this table it is interesting to note that $-\Delta H_p$ varies from 58.5 to 36.8 kJ mol^{-1}, only as a consequence of the positions of the two methyl groups in the lateral monomer substituent.

Assuming that the reaction of polymerization is first order with respect to the monomer concentration [4–7] and that the steady state conditions are established after the initial reaction period, the overall rate constant k' can be calculated according to

$$\ln[A/(A-a)] = k_p(2k_d f/k_t)^{1/2}\,[\mathrm{I}]^{1/2}\,\tau = k'\tau.$$

where k_p, k_d and k_t represent the propagation, initiator decomposition, and termination constants, f is the initiator efficiency and [I] its concentration, A the total area under the DSC curve, and a the partial area up to the time interval τ; k' is then the overall polymerization rate constant during the steady state period of the reaction. The values of k' obtained for all six monomers at various temperatures are presented in Table 2.

From Table 2 it can be seen that 3,4-DMPhMA is the fastest polymerizing monomer and 2,4-DMPhMA is the next to it but with considerably lower k' values. With the other four monomers the reaction was too slow at 348–353 K to obtain accurate reaction rate measurements. The slowest polymerizing monomer is 2,6-DMPhMA, with 2,3-DMPhMA next to it. The difference in reaction rates can be conveniently visualized and compared at 368 K and several higher temperatures. It can be expressed via the ratio of the reaction rate constants k'(3,4-DMPhMA)/k'(2,6-DMPhMA) which is 3.27 at 368 K but only 1.45 at 383 K, with a tendency to decrease still further for higher temperatures. Between 393 and 398 K, the values at the latter temperature resulting from extrapolation, all ratios k'/k' for any

TABLE 2

The temperature dependence of the k' overall rate constant of polymerization and the energy of activation E_a of six isomeric dimethyl phenyl methacrylates, DLP initiator concentration 0.05 mol l^{-1}

Temp. T (K)	Overall rate constant, k′ (10^3 s^{-1})					
	3,4-	3,5-	2,4-	2,5-	2,3-	2,6-
348	0.48	–	0.24	–	–	–
353	0.82	–	0.32	0.29	–	–
358	1.20	0.51	0.59	0.56	–	–
363	1.58	0.72	1.06	0.70	0.47	–
368	2.19	1.36	1.70	1.29	0.69	0.67
373	3.15	2.13	3.27	1.99	1.54	1.52
378	5.17	4.10	4.04	3.06	3.21	2.04
383	7.72	5.01	5.38	4.34	5.17	5.32
393	15.0	13.8	15.4	14.5	15.4	14.9
398 [a]	24.2	22.6	22.8	25.2	23.2	22.7
E_a (kJ mol^{-1})	84	112	106	101	146	158

[a] Rate constants at 398 K obtained by extrapolation.

combination of two different monomers approach the value of one. This observation is presented in Fig. 2 representing the temperature dependence of k' for four selected monomers. From the rate constants k'

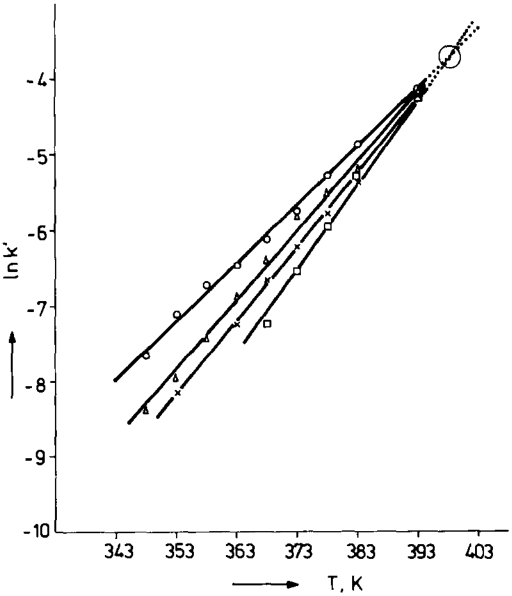


Fig. 2. The dependence of ln k' vs. temperature for four isomeric dimethyl phenyl methacrylates and the extrapolation to 400 K; (●) 3,4-DMPhMA, (△) 2,4-DMPhMA, (×) 2,5-DMPhMA, (□) 2,6-DMPhMA; intersection indicated with large circle.

presented in Table 2, the activation energy E_a of the polymerization reaction was calculated from the slopes of conventional Arrhenius plots. The activation energies obtained are presented in the last row of Table 2. It should be noticed that E_a values increase more or less in the same order as the rate constants k' decrease, as arranged in sequence in Table 2. Activation energies thus range from only 84 kJ mol^{-1} for 3,4-DMPhMA to a relatively very high value of 158 kJ mol^{-1} for 2,6-DMPhMA.

It is obviously assumed that all the differences observed result from the steric configuration of the six isomeric monomers investigated. The two methyl substituents in 3,4-DMPhMA are spaced far from the macroradical reaction propagation site, represented by one of the two carbon atoms of the C=C–group of the monomer having an unpaired electron. The steric configuration of this monomer enables easy access of the next monomer molecule to take part in the monomer addition step. No energy is consumed in overcoming any steric hindrance caused by the substituents; the reaction rate constant is therefore high and the exothermicity of the reaction reflected in $-\Delta H_p$ is also high. Consequently the activation energy is low, as reflected in the value of E_a observed.

In 2,6-DMPhMA the two methyl substituents are, on the contrary, closer to the reaction propagation site, causing considerable steric hindrance to approaching monomer molecules. The reaction is therefore slower, a part of the exothermic heat resulting from the opening of the double bond is consumed in overcoming the steric hindrance; $-\Delta H_p$ is therefore low but the activation energy is unexpectedly high. The other four monomers investigated fall within the limits of these two extremes. The phenomena observed must in part result also from different dipole/dipole interactions and hyperconjugation effects, caused by the different positions of the methyl substituents involved.

All effects discussed, reflected in the k' values and caused by steric hindrance and possibly other interactions in the system seem to vanish at still higher temperatures, i.e. when approaching the temperature of 400 K. At this temperature the thermal energy contained in the monomer molecule and macroradical seems to be sufficient to overcome easily barriers to the free rotation around bonds between atoms. Also, other interactions in the molecules vanish and restricted conformational areas at lower temperatures are now more probable. Therefore, the rates of propagation of all six monomers become practically equal. This general result is essentially in agreement with a previous publication from this laboratory [3] covering the interval 323–343 K, where a still higher ratio of k'(3,4-DMPhMA)/k'(2,6-DMPhMA) was observed, increasing with decreasing temperature.

ACKNOWLEDGEMENT

This work was supported by the Fund of Scientific Research of the Republic of Serbia.

REFERENCES

1 Lj. Vrhovac and J.S. Veličković, Makromol. Chem., 182 (1981) 2031.
2 Lj. Vrhovac, J.S. Veličković and D. Filipović, Makromol. Chem., 185 (1984) 1637.
3 Lj. Vrhovac, N. Djurasović and J.S. Veličković, submitted for publication.
4 T. Malavašić, I. Vizovisek, S. Lapanje and A. Može, Makromol. Chem., 175 (1974) 873.
5 A. Može, I. Vizovisek, T. Malavašić, F. Černec and S. Lapanje, Makromol. Chem., 175 (1974) 1507.
6 J.R. Embdon and J.B. Hunt, Anal. Chem., 45 (1973) 1804.
7 K. Issa, T. Nuno and D. Radic, Thermochim. Acta, 124 (1988) 263.