Journal of Thermal Analysis, Vol. 40 (1993) 735-740

DSC INVESTIGATION OF ISOTHERMAL BULK COPOLYMERIZATION OF ALKYLARYL METHACRYLATES

J. M. Filipovic, D. M. Petrovic-Djakov, Lj. P. Vrhovac and J. S. Velickovic

FACULTY OF TECHNOLOGY AND METALLURGY, UNIVERSITY OF BEOGRAD P.O.B. 494,
KARNEGIJEVA 4, YU-11000 BEOGRAD,YUGOSLAVIA

The free radical copolymerization of phenyl methacrylate (PhMA) with *o*-methylphenyl-methacrylate(*o*-MPhMA) and *o*-ethylphenyl methacrylate (*o*-EPhMA) was carried out and the enthalpies of copolymerization, overall rate constants and copolymerization parameters were determined for different molar ratios of comonomers in the temperature range 353–373 K.

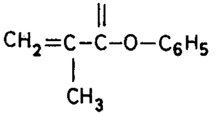
Keywords: alkylaryl methacrylates, copolymerization, DSC kinetics

Introduction

The kinetics of free radical polymerization of alkylaryl methacrylates has been studied extensivelly in our laboratory, using different techniques (dilatometry, gravimetry, DSC-measurements) [1, 3].

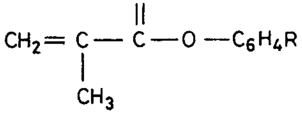
In the present work copolymerization kinetics for PhMA with *o*-MPhMA and *o*-EPhMA was investigated to determine the influence of methyl- or ethyl-substituent introduced in *o*-position in the phenyl ring of one of the comonomers, which can be represented by the general formula:

Monomer 1



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}C_6H_5$

Monomer 2



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}C_6H_4R$

where R – is – CH_3 (*o*-MPhMA) or –CH_2–CH_3 (*o*-EPhMA)

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

The synthesis of all monomers is described elsewhere [1, 2]. Monomer mixtures for copolymerization were prepared in molar ratio 3:1, 1:1 and 1:3, with 0.05 mol/l of AIBN. DSC curves were scaned isothermally on a Perkin–Elmer DSC-2 thermoanalyser in the temperature interval 348–373 K. Practically complete conversions were obtained in all runs.

Results and discussion

In Fig. 1 the course or polymerization of PhMA, *o*-MPhMA and their 1:1 mixture is presented. The reaction is faster and more exotherm for PhMA than in the case of *o*-MPhMA, and the rate of copolymerization is situated between these two boundary values.

For all other mixtures of PhMA with *o*-MPhMA and *o*-EPhMA the rate of copolymerization is proportional to the comonomer ratio, and lies between the values for parent comonomers.

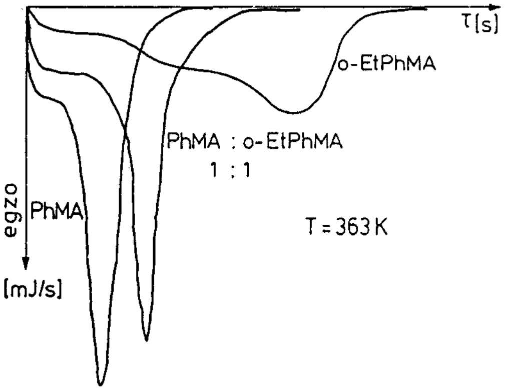


Fig. 1 Course of isothermal polymerization of PhMA and *o*-MPhMA and their copolymerization in molar ratio 1:1 at 363 K, with 0.05 mol/l of AIBN

Practically all curves show 4 stages of the reaction:

- the initial part
- the steady-state part
- the part where accelerated reaction proceeds, and
- the termination part.

Table 1 Enthalpy of copolymerization of PhMA with *o*-MPhMA and *o*-EPhMA and values for copolymerization parameter Ω

T /K	$-\Delta H_p$/kJ·mol^{-1}								
	Monomer			Monomer mixtures					
	PhMA	*o*-MPhMA	*o*-EPhMA	PhMA / *o*-MPhMA			PhMA / *o*-EPhMA		
				3:1	1:1	1:3	3:1	1:1	1:3
348	58.4	50.6	–	56.1	–	–	–	–	–
353	57.2	49.3	54.6	54.4	–	53.9	59.4	–	–
358	56.5	52.0	59.7	–	55.6	55.1	56.4	58.0	56.1
363	56.3	–	55.6	–	55.9	51.1	57.0	56.3	58.6
368	59.3	51.9	55.8	55.9	52.0	54.5	58.8	56.6	-
373	58.8	51.9	55.7	59.6	57.3	53.3	55.5	56.1	55.6
Mean value	57.8±1.2	51.1±1.0	56.4±1.1	56.5	55.2	53.6	57.4	56.9	56.8
Ω/kJ·mol^{-1}	–	–	–		3.0			-1.0	

Table 2 The overall rate constants (*k*) and activation energies for the copolymerization of PhMA with *o*-MPhMA and *o*-EPhMA

T/K	Monomer			Monomer mixtures					
	PhMA	*o*-MPhMa	*o*-EPhMA	PhMA / *o*-MPhMA			PhMA / *o*-EPhMA		
				3:1	1:1	1:3	3:1	1:1	1:3
348	2.10	1.11	–	–	–	–	–	–	–
353	2.71	1.54	1.17	2.42	2.04	–	2.49	2.28	1.95
358	3.55	2.73	2.40	3.83	3.49	2.89	3.26	3.23	2.65
363	4.95	3.67	3.39	4.75	4.46	4.17	4.26	4.00	3.89
368	6.24	5.37	5.20	6.07	5.90	5.89	5.99	5.88	5.58
373	9.09	9.57	8.08	10.58	10.59	9.26	10.07	9.09	8.90
E_a/kJ·mol^{-1}	62	82	81	63	66	76	64	73	78

Duration of individual stages depends on the composition of the monomer mixture. The gel-effect is most pronouced in the case of PhMA.

The polymerization enthalpies, calculated from the area under the DSC curves are presented in Table 1 as well as polymerization parameters.

There is a sharp increase in the rate of evolution of polymerization heat for conversions above 35% which is well explained by the kinetic model given by Dionisio and O'Driskoll [4].

The copolymerization parameters Ω [6] were calculated from:

$$\Omega = \Delta H_{12} + \Delta H_{21} - (\Delta H_{11} + \Delta H_{22})$$

where ΔH_{12} and ΔH_{21} are the copolymerization enthalpies, and ΔH_{11} and ΔH_{22} are the polymerization enthalpies of parent monomers.

The parameter Ω is independent of composition. Its value is low in both cases, but has a small positive value for the pair PhMA/MPhMA and a negative value for the pair PhMA/EPhMA.

The overall rate constants (k) were calculated from the total area of the curves (A) and the partial area (a) up to the time τ, for conversions up to 15%, for the first order reaction with respect to the monomer concentration. Values for k and activation energies are presented in Table 2.

Conclusions

In comparison of k values for PhMa and *o*-MPhMA, with the values for copolymers of different initial molar ratio, the influence of the $-CH_3$ group, which is introduced in the phenyl ring in *o*-position, must be borne in mind. The $-CH_3$ group restricts the free rotation of the planar phenyl group around O(ester)–C(aromatic) bond, due to the dipole-dipole interaction with the methyl group. This effect is slightly more pronounced in the case of *o*-EPhMA, where the dipole effect is combined with steric effects.

This is in a good agreement with the values of copolymerization parameter and energies of activation values.

References

1 Lj. Vrhovac and J. Velickovic, Makromoleculare Chemie, 182 (1981) 2031.
2 Lj. Vrhovac, J. Velickovic and D. Filipovic, Macromoleculare Chemie, 185 (1984) 1637.
3 D. Petrovic-Djakov, J. Filipovic, Lj. Vrhovac and J. Velickovic, 34th IUPAC Symposium, Prague, 1992.
4 J. Dionisio and K. O'Driskoll, J.Polym. Sci., Polymer Chemistry, 18 (1980) 241.
5 H. Sawada, Thermodynamics of polymerization, Marcel Dekker, New York 1976, p. 210.

Zusammenfassung — Es wurde die radikalische Kopolymerisation von Phenylmethacrylat (PhMA) mit *o*-Methylphenylmethacrylat (*o*-MPhMA) und *o*-Ethylphenylmethacrylat (*o*-EPhMA) durchgeführt und im Temperaturbereich 353-373 K für verschiedene Molverhältnisse der Komonomere die Enthalpien der Kopolymerisation, die resultierende Geschwindigkeitskonstante und die Kopolymerisationsparameter bestimmt.