

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Study of the Isothermal Bulk Polymerization of Methacrylic Acid and Some Methacrylic Acid Esters by Differential Scanning Calorimetry

T. Malavašič^a; U. Osredkar^a; I. Anžur^a; I. Vizovišek^a

^a Chemical Institute "Boris Kidric" and Department of Chemistry, University "Edvard Kardelj", Ljubljana, Yugoslavia

To cite this Article Malavašič, T. , Osredkar, U. , Anžur, I. and Vizovišek, I.(1986) 'Study of the Isothermal Bulk Polymerization of Methacrylic Acid and Some Methacrylic Acid Esters by Differential Scanning Calorimetry', *Journal of Macromolecular Science, Part A*, 23: 7, 853 – 860

To link to this Article: DOI: 10.1080/00222338608069477

URL: <http://dx.doi.org/10.1080/00222338608069477>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Study of the Isothermal Bulk Polymerization of Methacrylic Acid and Some Methacrylic Acid Esters by Differential Scanning Calorimetry

T. MALAVAŠIČ, U. OSREDKAR, I. ANŽUR, and I. VIZOVIŠEK

Chemical Institute "Boris Kidric" and Department of Chemistry
University "Edvard Kardelj"
Ljubljana, Yugoslavia

ABSTRACT

The course of the isothermal bulk polymerization of methacrylic acid and some methacrylic acid esters differing in the length of the ester group was studied by differential scanning calorimetry at different temperatures. The enthalpies of polymerization, the residual monomer content, the overall reaction rate constants, and the overall activation energies were calculated. The molecular weight averages of the synthesized polymers before and after the gel effect were measured by gel permeation chromatography.

INTRODUCTION

Several studies of the polymerization of methyl methacrylate have been made, and many models were developed to explain the onset of the gel effect after the initial stationary polymerization [1-9]. The gel effect phenomenon in the polymerization of some alkyl methacrylates was observed by many other investigators as well [10-16]. In the present work, the isothermal polymerization of methacrylic acid (MA), methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), and hexyl methacrylate (HMA) was studied by

differential scanning calorimetry (DSC). Our already published method [17-20] was used for the evaluation of the DSC curves. The aim of the work was to determine the influence of the length of the alkyl group in some alkyl methacrylates on the course and kinetics of their polymerization. Therefore, monomers were selected differing only in the number of C atoms in the linear ester chain. The molecular weight averages of the corresponding polymers (PMMA, PEMA, PBMA, and PHMA) were determined.

EXPERIMENTAL

Materials

Monomers were freed of inhibitor and distilled under nitrogen at reduced pressure. The initiator 2,2'-azoisobutyronitrile (AIBN) was recrystallized from absolute ethanol and stored in the dark at -25°C .

Method

The isothermal radical polymerization of MA, MMA, EMA, BMA, and HMA was investigated at 353, 358, 363, and 368 K with a Perkin-Elmer DSC-2 differential scanning calorimeter. To initiate the polymerization, 50 mmol/L of AIBN was added. The enthalpies of the reaction and the overall rate constants were calculated from the areas between the DSC curves and the baseline, which was obtained by back-extrapolation of the straight line recorded after the polymerization was finished. The calorimeter was calibrated with the melting enthalpy of indium. The DSC curves were digitalized on line and processed by a computer.

The molecular weight averages of the polymerization products at the stationary phase of the reaction and at the end of the polymerization were measured by gel permeation chromatography (GPC) relative to polystyrene standards. A Varian 8500 Model gel chromatograph equipped with μ -Styragel columns (pore sizes 10^{-5} , 10^{-6} , 10^{-7} , and 5×10^{-8} m) was used with a differential refractometer as detector. The measurements were performed in tetrahydrofuran solution.

RESULTS AND DISCUSSION

The course of the isothermal bulk polymerization of MA, MMA, EMA, BMA, and HMA at 363 K is presented in Fig. 1. It can be seen that the courses of polymerization of MMA, EMA, and BMA are similar. After the initially stationary reaction, a well-expressed gel effect sets in. However, with increasing length of the alkyl group in the

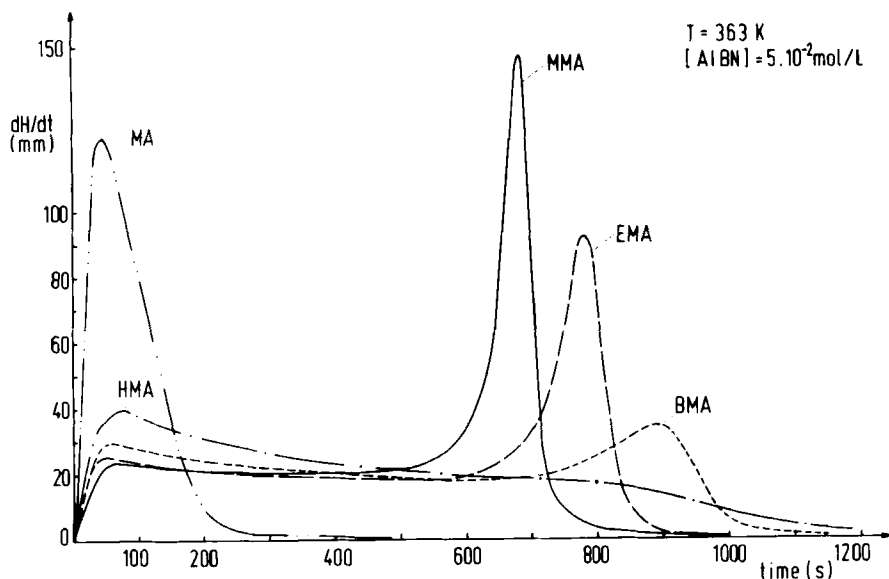


FIG. 1. Isothermal polymerization of MA, MMA, EMA, BMA, and HMA at 363 K in the presence of 50 mmol/L of AIBN.

methacrylic acid ester, the intensity of the gel effect decreases and the conversion at the onset of the gel effect increases [17]. In the polymerization of HMA, the gel effect cannot be observed. In contrast, in the polymerization of MA the gel effect starts immediately after the beginning of the reaction. Compared to methacrylic acid esters under the same conditions, the reaction of MA ends very quickly.

The shift of the onset of the gel effect to higher conversion and its suppression in the polymerization of higher methacrylic acid esters cannot be explained by the theory of diffusion-controlled termination in highly viscous media as a consequence of increasing viscosity of the monomers. However, our measurements agree with the findings of Cardenas and O'Driscoll [16] and with the results of Burnett and Duncan [22].

The observed delay and the suppression of the gel effect as well as the complete conversion of monomer in the polymerization of higher methacrylic acid esters support the suggestion [2, 14, 25, 26] that segmental rearrangement is the rate-determining process in diffusion-controlled termination, since the mobility of the polymer chain becomes higher with increasing length of the alkyl group as a consequence of the shielding of the carbonyl by the alkyl group. The lowering of the glass transition temperature of polyalkyl methacrylates [27] was explained in the same way.

TABLE 1. Polymerization Enthalpies

Temperature, K	Polymerization enthalpy, kJ/mol ^a				
	MA	MMA	EMA	BMA	HMA
353	38.8	55.2	60.2	60.3	60.4
358	38.9	55.7	61.1	61.4	60.0
363	39.8	56.8	59.5	62.8	59.3
368	39.5	57.3	60.1	59.8	58.9

^aNot corrected for unreacted monomer.

DSC measurements confirm that the initial polymerization rates increase with the length of the ester group. This can be explained in terms of the inductive effect [24].

The polymerization enthalpies for the same monomer at different temperatures are within the limits of experimental error, estimated to be $\pm 5\%$ (Table 1). The polymerization enthalpy for MA is much lower than the literature data [21].

The unreacted monomer content was determined by heating the polymerization products from 333 to 423 K [18]. It was found that it was the highest for MA (6% at 363 K), smaller for MMA and EMA (3.4% at 363 K), and that it decreased to zero for BMA and HMA.

The overall rate constants of polymerization,

$$k' = k_p (fk_d[I_0]/k_t)^{1/2},$$

were calculated from the linear part of the curves in plots of $\ln A/(A-a)$ vs time, where A is the total area and a the partial area between the DSC curves and the baseline (Table 2). The parameters k_p , k_d , and k_t are the rate constants for propagation, initiator dissociation, and termination; f is the initiator efficiency; and $[I_0]$ is its initial concentration. The values for MA could not be calculated in the same way because of the nonexistence of the stationary state at the beginning of the polymerization. The rate constants k' increase linearly with increasing temperature and increasing length of the ester group in the monomer. This is in agreement with the results of Burnett and Duncan [22]; Otsu, Ito, and Imoto [15, 23]; and Cardenas and O'Driscoll [16] (Fig. 2).

The overall Arrhenius activation energies for polymerization were calculated from the overall rate constants. The values are practically the same for all the monomers studied. The values are given in Table 2.

TABLE 2. Rate Data for Polymerization and Molecular Weight Averages before and after Gel Effect

Monomer	Overall rate constants, $k' \times 10^3, s^{-1}$				Activation energy, kJ/mol	Relative polymer molecular weight $M \times 10^{-4}$	
	353 K	358 K	363 K	368 K		Before gel effect	After gel effect
MMA	0.46	0.67	0.95	1.34	76.8	4.5	9.1
EMA	0.52	0.74	1.04	1.50	76.3	4.9	9.4
BMA	0.70	1.01	1.43	1.98	76.8	7.4	10.0
HMA	0.89	1.27	1.82	2.57	76.5	8.7	10.5

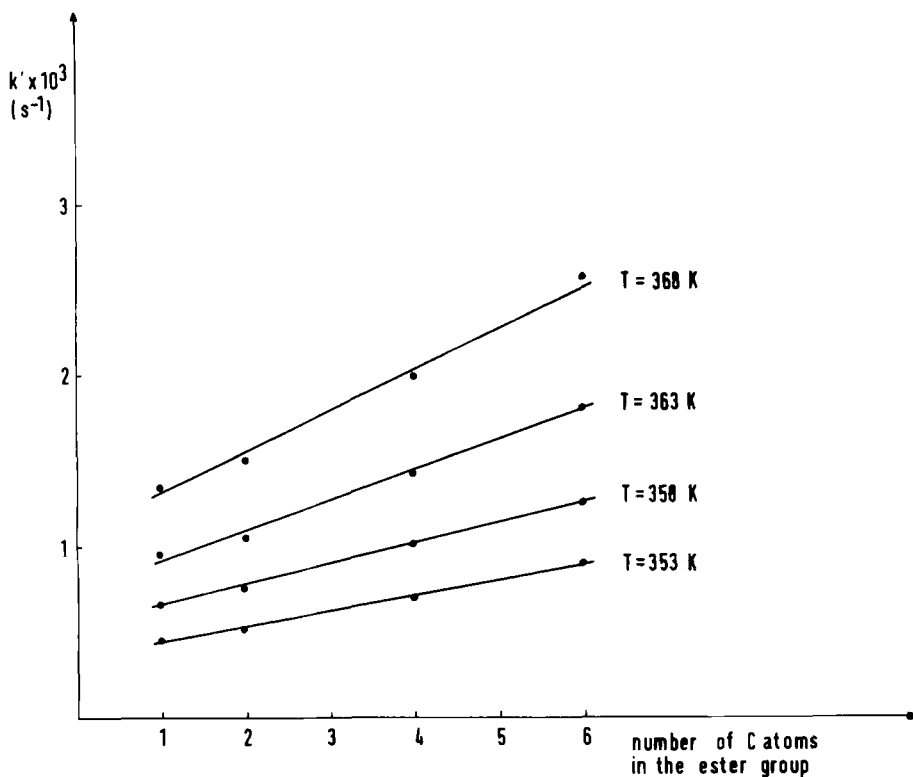


FIG. 2. Overall rate constants as a function of the number of C atoms in the linear ester group at different temperatures.

Molecular weight measurements could not be done for poly(methacrylic acid) since there is no suitable solvent. Average molecular weights for the other polymers are given in Table 2. For PMMA and PEMA, \bar{M} before the gel effect is almost half that after the gel effect. This difference becomes smaller with increasing length of the alkyl group; for PHMA the values are very close. For PBMA, \bar{M} after the gel effect was also measured as a function of the reaction temperatures (Table 3). As expected, the values decrease with increasing temperature.

CONCLUSIONS

Measurements of the course of polymerization of some methacrylic acid esters, differing in the length of the linear ester group only, support the hypothesis that segmental rearrangement is the rate-determining

TABLE 3. Dependence of Molecular Weight Averages on Temperature for PBMA

Polymerization temperature, K	Molecular weight average $M \times 10^{-4}$ after gel effect
353	14.8
358	12.2
363	10.0
368	9.3

ing process in diffusion-controlled termination. The rotation of the polymer chain becomes easier with increasing length of the ester group due to shielding of the carbonyl group by the alkyl group and causes a delay in the onset of the gel effect and its suppression. The overall polymerization rate constants increase with an increasing number of C atoms in the ester group. The difference in molecular weight average before and after the gel effect diminishes with increasing length of the ester group, i.e., with the suppression of the gel effect.

REFERENCES

- [1] E. Trommsdorff, H. Koehle, and P. Lagally, Makromol. Chem., **1**, 169 (1948).
- [2] J. N. Cardenas and K. F. O'Driscoll, J. Polym. Sci., Polym. Chem. Ed., **14**, 883 (1976).
- [3] J. M. Dionisio and K. F. O'Driscoll, Ibid., **18**, 241 (1980).
- [4] T. J. Tulig and M. Tirrell, Macromolecules, **14**, 1501 (1981).
- [5] T. J. Tulig and M. Tirrell, Ibid., **15**, 459 (1982).
- [6] D. T. Turner, Ibid., **10**, 221 (1977).
- [7] H. B. Lee and D. T. Turner, Ibid., **10**, 226 (1977).
- [8] K. A. High, H. B. Lee, and D. T. Turner, Ibid., **12**, 332 (1979).
- [9] W. Y. Chiu, G. M. Carratt, and D. S. Soong, Ibid., **16**, 348 (1983).
- [10] G. M. Burnett, P. Evans, and H. W. Melville, Trans. Faraday Soc., **49**, 1096, 1105 (1953).
- [11] D. H. Grant and N. Grassie, Ibid., **55**, 1042 (1959).
- [12] G. G. Cameron, D. H. Grant, and N. Grassie, J. Polym. Sci., **36**, 173 (1959).
- [13] G. M. Burnett and G. J. Duncan, Makromol. Chem., **51**, 154, 171 (1961).
- [14] A. M. North and G. A. Reed, J. Polym. Sci., Part A, **1**, 1311 (1963).
- [15] T. Otsu, T. Ito, and M. Imoto, Ibid., **2**, 2901 (1964).

- [16] J. N. Cardenas and K. F. O'Driscoll, J. Polym. Sci., Polym. Chem. Ed., **15**, 2097 (1977).
- [17] T. Malavasic, U. Osredkar, I. Anzur, and I. Vizovisek, J. Therm. Anal., **29**, 697 (1984).
- [18] T. Malavasic, I. Vizovisek, S. Lapanje, and A. Moze, Makromol. Chem., **175**, 873 (1974).
- [19] T. Malavasic, I. Vizovisek, U. Osredkar, and I. Anzur, J. Polym. Sci., Polym. Symp., **69**, 73 (1981).
- [20] T. Malavasic, U. Osredkar, I. Anzur, and I. Vizovisek, J. Macromol. Sci.-Chem., **A19**, 987 (1983).
- [21] K. G. McCurdy and K. J. Laidler, Can. J. Chem., **42**, 818 (1964).
- [22] G. M. Burnett and G. L. Duncan, Makromol. Chem., **51**, 154, 177 (1961).
- [23] T. Otsu, T. Ito, and M. Imoto, J. Polym. Sci., Part B, **3**, 113 (1965).
- [24] K. G. McCurdy and K. J. Laidler, Can. J. Chem., **42**, 825 (1964).
- [25] S. W. Benson and A. M. North, J. Am. Chem. Soc., **84**, 935 (1962).
- [26] R. D. Burkhart, J. Polym. Sci., Part A, **3**, 883 (1965).
- [27] W. Cooper, "Synthetic Elastomers," in Encyclopedia of Polymer Science and Technology, Vol. 5 (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Wiley-Interscience, New York, 1966, p. 435.

Received April 18, 1985

Revision received July 23, 1985