Polymer Bulletin 5, 551–556 (1981)

Polymer Bulletin

Microcalorimetric Investigation of High Conversion Polymerization

E. Takács and J. Dobó

Research Institute for Plastics, Hungaria krt. 114, 1950 Budapest, Hungary

Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

Abstract

A Calvet-type microcalorimeter was used for direct and continuous measurement of the rate of polymerization up to high conversion. The polymerization rate curve of methylmethacrylate /MMA/ was analyzed, and the effect of poly/vinyl-chloride/ /PVC/ on the polymerization of MMA was investigated.

Introduction

Calorimetry is a widely used method in polymer chemistry. Differential scanning calorimeter /DSC/ is often used to study phase transitions in polymers, thermodynamic constants /e.g. specific heat/, heat of thermal degradation of polymers, heat of initiator decomposition and so on.

DSC is also suitable to investigate polymerization reactions. In that case mostly a modified instrument is used at constant temperature to follow the rate of polymerization. Different kinetic parameters can be calculated from the rate curves, such as heat of polymerization, rate constants /HORIE 1968, HORIE 1969, HORIE 1970, HORIE 1975, BEVINGTON 1977, MOORE 1975, WRIGHT 1978/.

Calvet-type microcalorimeter has been used for investigation of grafting of styrene and MMA to air-pre-irradiated polyethylene /BARIC 1974, DOBÓ 1975, BARIC 1979/. This type of calorimeter is particularly suitable for following both grafting and high conversion block polymerization.

In our laboratory a modified Calvet-type microcalorimeter operated at constant temperature was succesfully used for direct and continuous measurement of the rate of radiation polymerization of MMA and of the rate of radiation grafting of methylmethacrylate to PVC powder.

Experimental

A modified Calvet-type microcalorimeter was constructed in our laboratory especially for radiation chemical works. This type of calorimeter shows directly the rate

0170-0839/81/0005/0551/$01.20

of heat evolution corresponding to the rate of reaction. The sample holders are 1,8 cm^3 glass ampules, sealed under argon atmosphere.

The MMA monomer supplied by Merck Schuchardt /for synthesis/ was twice destilled before use. Emulsion polymerized PVC type Halvic 122 was supplied by Solvay. The polymerization of MMA was initiated by a $3,7 \cdot 10^{13}$ Bq /1000 Curie/ Co 60 source at a dose rate of 500 Gy /50 krd/h/.

Results and Discussion

The rate of radiation polymerization of MMA is shown on Figure 1. together with the energy of activation as a function of conversion.

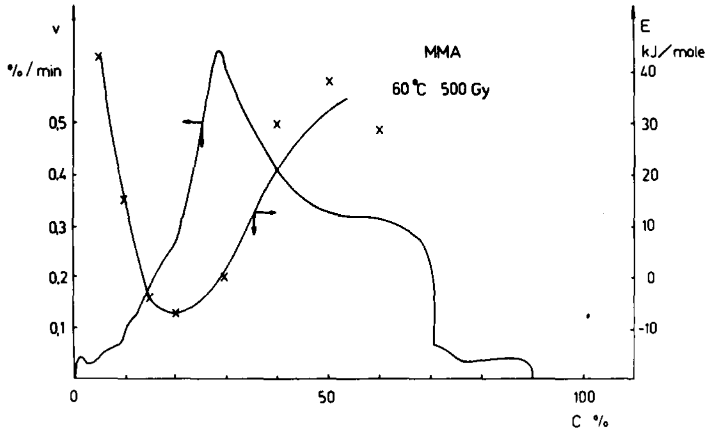

Fig. 1. The polymerization rate and the overall energy of activation of MMA as a function of conversion at 60°C. Dose rate 500 Gy /50 krd/hour/.

The rate of polymerization increases virtually from the beginning of the reaction. This is connected with the fact that the rate of initiation of radiation polymerization continuously increases because the polymer, formed, has a higher radiation sensitivity than the monomer.

The gel effect due to diffusion-controlled termination /TROMMSDORF 1948/ starts at about 20% conversion and the rate reaches a maximum at about 30% conversion.

After the peak a shoulder appears on the curve. Thus, between about 45 and 70% conversion, the rate of polymerization is nearly constant.

Finally, the polymerization of MMA is abruptly slowed down at a conversion where the segmental diffusion of the polymeric chain ends and even the translational diffusion of the monomer are suppressed because of the transition of the polymer-monomer system from a viscous liquid to a glass.

The glass transition temperature of a polymer-monomer mixture can be calculated by the following equation first derived by Gordon and Taylor /GORDON 1952/ and developed by Kelley and Bueche /KELLEY 1961/, assuming the additivity of the free volumes of the constituents.

$$T = \frac{\Delta\alpha_p \Phi_p T_{gp} + \Delta\alpha_m (1 - \Phi_p) T_{gm}}{\Delta\alpha_p \Phi_p + \Delta\alpha_m (1 - \Phi_p)} \qquad /1/$$

where $\Delta\alpha_p$ and $\Delta\alpha_m$ respectively are the difference between the volume expansion coefficients of the polymer and monomer in melt and in a glassy state; Φ_p is the volume fraction of the polymer in the system; T_{gp} and T_{gm} respectively are the glass transition temperature of the polymer and monomer. On setting T in eq /1/ equal to the polymerization temperature and using a value of $T_{gm} = -106^\circ C$ /CHAPIRO 1966/ together with $\Delta\alpha_m = 1.10^{-3}/^\circ C$ $T_{gp} = 113^\circ C$ $\Delta\alpha_p = 4{,}8 \cdot 10^{-4}/C^\circ$ /BUECHE 1962/ the volume fraction of the polymer at which the system shows a transition from a viscous liquid to glass was calculated. The calculated values of Φ_p agree quite well with the final conversion value obtained from the calorimetric data shown in Table 1.

TABLE 1

The volume fraction of the polymer at the glass transition temperature

Temperature °K	Φ_p calculated %	Φ_p measured %
313	82,0	80,0
323	85,9	85,0
333	88,5	90,0
343	91,2	92,0
353	93,0	93,8

From the reaction rate, measured at different temperatures the overall energy of activation was calculated. Fig. 1. shows the calculated values.

The effect of PVC powder type Halvic 122 on the rate of polymerization of MMA was then investigated. PVC and MMA was mixed in different ratios and the polymerization rate curves were obtained by microcalorimeter. From the measured rate curves the final conversions were calculated. Figure 2. shows the maximum polymerization rates together with the final conversions as a function of the composition of the PVC-MMA mixture.

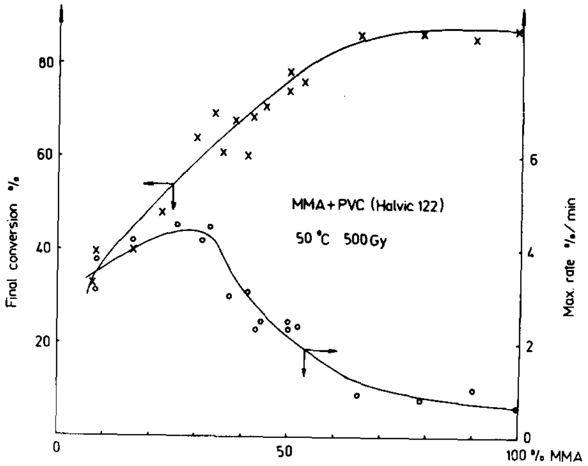

Fig. 2. The maximum values of the calorimetric rate curves and final conversions as a function of PVC:MMA ratio. Measured at 50°C and 500 Gy /50 krd/hours/.

At small MMA content up to 30% the maximum rate of polymerization is about 5 times higher than that of pure MMA. The PVC immobilizes the growing methacrylic radicals resulting in a diffusion controlled chain termination. Besides, the rate of initiation is increased by radicals occuring in the PVC chains during irradiation. Both these effects increase the overall rate of the reaction. These two effects are stronger then the diluting effect of the PVC and cause high rate maximum. This maximum is rather sharp, as it is shown in Fig. 3A.

The autoacceleration occurs right at the beginning of the reaction and on the other hand, the reaction rate decreases at small conversion. Increasing the amount of MMA the above mentioned accelerating effects decrease resulting in a lower rate maximum. The rate curve broadens out /Fig. 3B/ and above 50% MMA content both the final conversion and the rate maximum is the same as those of the pure monomer.

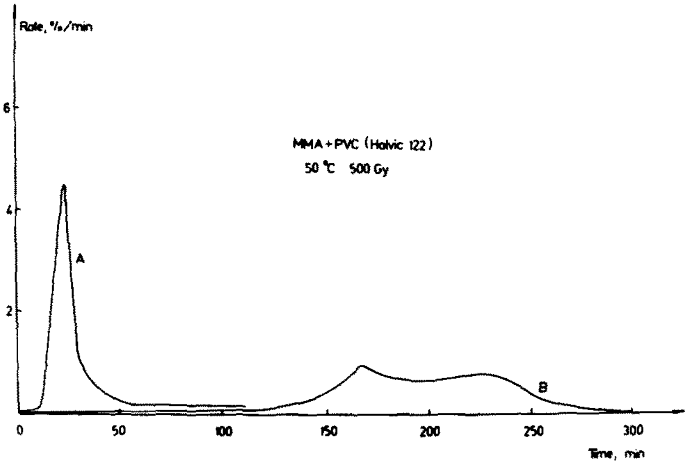

Fig. 3. Calorimetric rate curve of MMA in the presence of PVC powder type Halvic 122.

A - PVC + 33% MMA
B - PVC + 65% MMA

50°C, 500 Gy /50 krd/hours/.

<u>REFERENCES</u>

1. HORIE, K. at al., J. Polymer Sci. Part A-1, 6, 2663 /1968/
2. HORIE, K., J. Polymer Sci. Part A-1, 7 , 2561 /1969/
3. HORIE, K., J. Polymer Sci. Part A-1, 8, 2839 /1970/
4. HORIE, K. at al., J. Polymer Sci., Part A-1,13, 445 /1975/
5. BEVINGTON, J.C. at al., Polymer 18, 73 /1977/
6. MOORE, J.E. at al., Am. Chem. Soc. Coating and Plastics Preprints 35/1/, 239 /1975/
7. WRIGHT, F.R. and HICKS, G.W., Polymer Eng. Sci. 18/5/, 379 /1978/
8. BARIC, M. at al., Proc. IUPAC Macromol. Symp. 1974, Madrid, p 507
9. DOBÓ,J., Magyar Kémikusok Lapja 30, 236 /1975/
10. BARIC, M. at al., Croat. Chem. Acta, 52/3/, 223 /1979/
11. GORDON, M. and TAYLOR, J.S., J. Appl. Chem. 2, 493 /1952/
12. KELLEY, F.N. and BUECHE,F., J. Polymer Sci. 5, 549 /1961/
13. BUECHE, F., Physical Properties of Polymers, New York, Interscience, 1962

14. TROMMSDORFF, E. at al., Makromol. Chem. 1, 169 /1948/
15. CHAPIRO, A. and NAKASHIO, S., J. Chem. Phys. 63, 1031 /1966/

Received September 14, accepted September 24, 1981