four-bond A′/B coupling constants are significantly less than the vicinal B/C coupling constants, so the B/C cross-peaks are observed at the expense of the A′/B cross-peaks.

Registry No. PVF, 24981-14-4.

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Macroporous Gels. 5. A Differential Scanning Calorimetry Study of the Formation of Macroporous Gels Containing Trimethylolpropane Trimethacrylate

J.-E. Rosenberg and P. Flodin*

Department of Polymer Technology, Chalmers University of Technology,
S-412 96 Gothenburg, Sweden.

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ABSTRACT: The free radical homopolymerization of trimethylolpropane trimethacrylate (TRIM) and the free radical copolymerization of TRIM and methyl methacrylate (MMA) in solution were studied by DSC. The kinetic order of reaction and the activation energy were determined by both isothermal and dynamic measurements. Calculations of the activation energy from isothermal and dynamic measurements were in good agreement, as were results from homopolymerization and copolymerization experiments (about 20 kcal/g). The reactions were shown to be of nearly first order, which is in fair agreement with the results of previous NMR measurements.

Introduction

The polymerization of trimethylolpropane trimethacrylate (TRIM) in a solvent often results in macroporous gels.[1,2] It is possible to vary the structure of these resins by polymerization in different solvents and by copolymerization with suitable monomers.[2,3]

Differential scanning calorimeter (DSC) is a powerful tool in evaluating the kinetics of a polymerization. Simple methods for calculating the activation energy and the kinetic order of reaction from both dynamic and isothermal measurements have been described in the literature.[6-9]

The purpose of this paper is to study the formation of poly(TRIM) through the evolution of heat during the polymerization. Performing a polymerization in a DSC apparatus makes it possible to follow the whole reaction continuously. The behavior of the TRIM homopolymerization and the TRIM-MMA copolymerization in two different solvents (toluene and ethyl acetate) will be described. This is important for the understanding of polymerizations in which large amount of TRIM monomer are present.

A comparison of the results obtained with a previous investigation of the polymerization of trimethylolpropane trimethacrylate by ^{1}H FT NMR[4] will also be made.

Experimental Section

Polymerization (DSC Studies). In homopolymerization experiments, trimethylolpropane trimethacrylate (TRIM, technical quality containing more than 98% TRIM from Merck AG and Alfa Products) was mixed with a solvent (toluene or ethyl acetate, analytical grade), while in the copolymerization experiments methyl methacrylate (MMA, analytical grade) was also included. The mixture was transferred into a 50-mL hypo-vial containing 0.1% (w/w) azobis(isobutyronitrile) (AIBN, analytical grade). In the following, mixtures will be given in volume percent.

Nitrogen gas was bubbled through the solution for at least 1 min and then the vial was sealed. A sufficient amount (about 20 mg) of the solution was then transferred into a DSC high-pressure steel sample cup (Perkin-Elmer, no. 319-0218) and placed in the DSC cell.

Kinetic Measurements with DSC. The in situ DSC experiments were carried out in two different ways, by dynamic (scanning) and by isothermal measurements. The isothermal measurements were performed at four different temperatures, 343, 348, 353, and 358 K. The four heating rates in the dynamic measurements were 0.62, 1.25, 2.5, and 5.0 K/min. Indium was used for temperature and calorimetric calibration. All experiments were carried out under a constant flow of nitrogen through the DSC cell. An empty high-pressure steel sample cup was used as a reference. The instrument used for the measurements was a Perkin-Elmer DSC-2.

Results and Discussion

Theoretical Considerations. By DSC one measures the rates of heat absorption or evolution (dH/dt) of a sample compared to a reference when the temperature is raised at a constant rate. It is also possible to make the measurements under isothermal conditions. It is possible to calculate the activation energy and the kinetic reaction order of the polymerization reaction by evaluating both the dynamic and the isothermal (DSC) thermograms.[5-9] The first method was partly proposed by Barton[6] and is based on multiple isothermal experiments at different

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* To whom correspondence should be addressed.

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temperatures. The kinetic equation is given by the following expression:

$$d\alpha/dt = k\,f(\alpha) \tag{1}$$

where $d\alpha/dt$ is the rate of reaction, k is the rate constant, and α is the degree of conversion. The reaction rate constant k can be expressed as

$$k = A \exp(-E/RT) \tag{2}$$

where A is the frequency factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. Equation 1 can then by rewritten as

$$d\alpha/dt = A \exp(-E/RT)\,f(\alpha) \tag{3}$$

or

$$\ln \frac{d\alpha}{dt} = \ln\,[A\,f(\alpha)] - \frac{E}{RT} \tag{4}$$

In DSC measurements the amount of heat evolved is proportional to the degree of conversion:

$$\alpha = H_p/H_t \tag{5}$$

where H_p is the partial heat of the reaction and H_t is the total heat of reaction. The reaction rate can then be expressed as follows:

$$r = \frac{d\alpha}{dt} = \frac{1}{H_t}\frac{dH_p}{dt} \tag{6}$$

Equation 4 can then be rewritten as

$$\ln r = \ln \left[\frac{1}{H_t}\frac{dH_p}{dt}\right] = \ln\,[A\,f(\alpha)] - E/RT \tag{7}$$

If $f(\alpha)$ is independent of the temperature, E can be calculated from isothermal measurements at various temperatures by plotting $\ln\,[1/H_t\ dH_p/dt]$ versus $1/T$ at a fixed conversion (α = constant). The line obtained should have a slope of $-E/R$.

A conventional assumption is that $f(\alpha) = (1-\alpha)^n$ where n is the kinetic order of reaction.[5-7] Equation 7 can then be written as

$$\ln r = \ln A - E/RT + n \ln\,(1-\alpha) \tag{8}$$

By using eq 8, it is possible to calculate the kinetic order of the reaction from one isothermal measurement because the term $\ln A - E/RT$ stays constant if the temperature is not changed.

A plot of $\ln r$ versus $\ln\,(1-\alpha)$ at different conversions then results in a straight line with a slope equal to n.

A second method, which gives an alternative approach to the derivation of the activation energy, is to use the result from multiple dynamic DSC curves obtained at various scan rates.[8] This method assumes that the reaction rate reaches a maximum when dH_p/dT attains its maximum value and the slope of the curve is equal to zero. With these assumptions Kissinger[8] obtained the following equation for the reaction:

$$\frac{d[\ln\,(dT/dt)]}{d(1/T_p)} = -\frac{E}{R} - 2T_p \tag{9}$$

where T_p is the peak temperature. Plotting $\ln\,(dT/dt)$ versus $1/T_p$ for several DSC curves obtained at various scan rates would then result in a straight line with the slope $-E/R$ when $E/R \gg 2T_p$. In this case it is also assumed that the reaction order, n, remains constant throughout the reaction.

Table I
General Results from Isothermal Experiments[a]

polymeriztn system	temp, °C	time, min t_i	t_p	t_f
TRIM-TOL	70	23	41	94
TRIM-TOL	75	22	35	68
TRIM-TOL	80	24	36	55
TRIM-TOL	85	0	10	35
TRIM-ETAC	70	16	28	93
TRIM-ETAC	75	12	23	73
TRIM-ETAC	80	1	9	37
TRIM-ETAC	85	0	8	24
TRIM-MMA-TOL	70	17	48	130
TRIM-MMA-TOL	75	15	35	78
TRIM-MMA-TOL	80	2	19	56
TRIM-MMA-TOL	85	1	12	44
TRIM-MMA-ETAC	70	36	47	105
TRIM-MMA-ETAC	75	22	32	73
TRIM-MMA-ETAC	80	18	26	50
TRIM-MMA-ETAC	85	1	12	35

[a] The homopolymerization mixture consisted of 30% TRIM and 70% solvent [toluene (TOL) or ethyl acetate (ETAC)]. The copolymerization mixture consisted of 30% monomer (80% TRIM and 20% MMA) in 70% solvent (toluene or ethyl acetate).

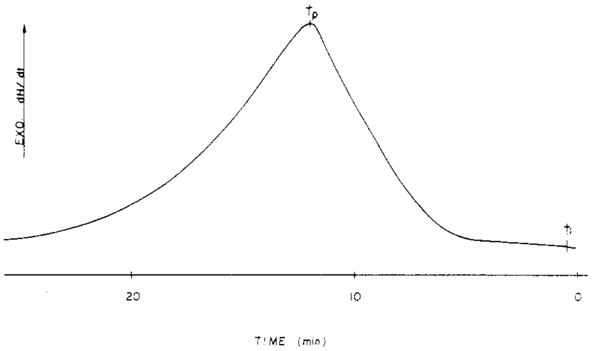

Figure 1. Typical isothermal DSC thermogram from a TRIM–MMA copolymerization in the presence of toluene (temperature = 85 °C; monomer:solvent = 30:70; the monomer mixture consisted of 80% TRIM and 20% MMA).

Isothermal Measurements. The results from the isothermal experiments are presented in Table I. The times t_i, t_p, and t_f represent the initial, the peak, and the final times of the polymerization. As expected all three times decrease with increasing temperature. The time that affected the reproducibility most was the initial time (t_i). This was probably due to the diffusion of oxygen into the sample (inhibition of the reaction) when the polymerization mixture was transferred into the DSC sample cup.

A typical isothermal DSC thermogram of a TRIM–MMA copolymerization at 85 °C is shown in Figure 1. From this thermogram it is possible to follow the evolution of heat during the polymerization. At the start, the polymerization proceeds slowly, but after about 4 min a break point can be observed. After the break point there is a rapid increase in the heat evolution until a maximum is reached whereupon the curve slowly returns to the base line. The heat of reaction (H_t) in the isotherm was about the same (125 (±10%) J/g) for all systems except the TRIM/MMA copolymer system polymerized in toluene, which had a H_t values of about 158 J/g. None of the H_t values showed any dependence on the polymerization temperature.

Previous experiments made by visual observations of the gel point together with NMR observations show that the conversion when gelation occurred was about 3–4%, which was unexpectedly low.[4] If a comparison is made between the NMR investigations and the DSC results, it is possible

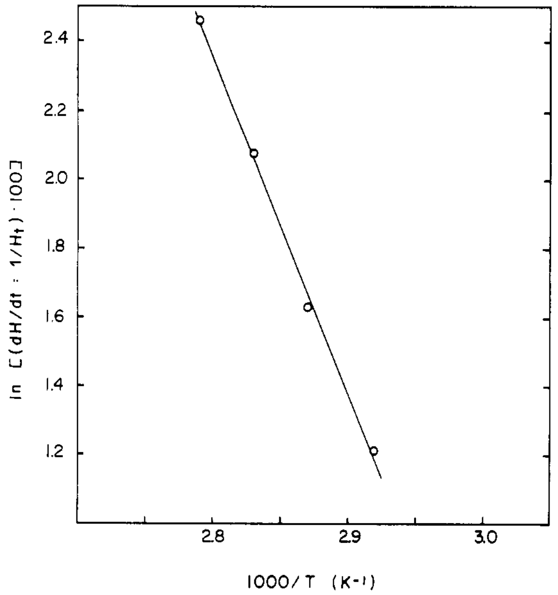

Figure 2. Relationship between ln [dH/dt 1/H_t] and 1/T for four different isothermal measurements (TRIM-MMA copolymerization in the presence of ethyl acetate; monomer:solvent = 30:70; the monomer mixture consisted of 80% TRIM and 20% MMA). Application of eq 7.

Table II
Calculation of the Activation Energy and the Kinetic Order of Reaction According to Equations 7 and 8 for Two Homopolymerization Systems[a] and for Two Copolymerization Systems[b]

polymeriztn system	activation energy kcal/mol	activation energy kJ/mol	kinetic order of reactn
TRIM-TOL	20.0	83.8	1.0
TRIM-ETAC	22.7	95.3	0.9
TRIM-MMA-TOL	18.0	75.4	0.8
TRIM-MMA-ETAC	19.3	81.0	0.7

[a] 30% TRIM and 70% solvent (toluene or ethyl acetate). [b] 30% monomer mixture consisting of 80% TRIM and 20% MMA in 70% solvent (toluene or ethyl acetate).

to conclude that the break point in the DSC thermogram occurs in connection with the gelation of the system.

The thermograms obtained at different temperatures were analyzed by using the first method through the application of eq 7 and 8. A typical plot resulting from the application of eq 7 is shown in Figure 2. The activation energies as well as the kinetic order of reaction calculated are presented in Table II. The activation energies appear to have about the same value for all four systems used. A slight difference occurs, however, in the kinetic order of reaction which is lower for the copolymerization reactions. The calculations made from eq 7 and 8 also confirm that the assumptions of $f(\alpha)$ are valid.

Dynamic Measurements. The results from the dynamic experiments are presented in Table III. T_i and T_p represent the initial and the peak temperatures. The peak temperature as well as the initial temperature increase with increasing heating rate. The initial temperatures, which are least reproducible, are the ones at which the reaction becomes rapid enough to be detected by DSC.

Table III
General Results from Dynamic Experiments[a]

polymeriztn system	heating rate, K/min	temp, °C T_i	temp, °C T_p
TRIM-TOL	0.62	65	76
TRIM-TOL	1.25	68	88
TRIM-TOL	2.5	81	104
TRIM-TOL	5.0	83	103
TRIM-ETAC	0.62	69	84
TRIM-ETAC	1.25	52	90
TRIM-ETAC	2.5	66	102
TRIM-ETAC	5.0	86	104
TRIM-MMA-TOL	0.62	61	85
TRIM-MMA-TOL	1.25	67	88
TRIM-MMA-TOL	2.5	72	95
TRIM-MMA-TOL	5.0	82	102
TRIM-MMA-ETAC	0.62	74	84
TRIM-MMA-ETAC	1.25	78	90
TRIM-MMA-ETAC	2.5	80	100
TRIM-MMA-ETAC	5.0	85	110

[a] The homopolymerization mixture consisted of 30% TRIM and 70% solvent [toluene (TOL) or ethyl acetate (ETAC)]. The copolymerization mixture consisted of 30% monomer (80% TRIM and 20% MMA) in 70% solvent (toluene or ethyl acetate).

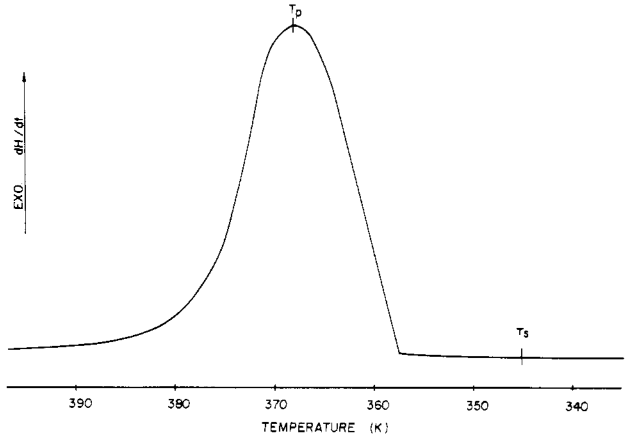

Figure 3. Typical dynamic DSC thermogram from a TRIM-MMA copolymerization in the presence of toluene (scanning rate = 2.5 K/min; monomer:solvent = 30:70; the monomer mixture consisted of 80% TRIM and 20% MMA).

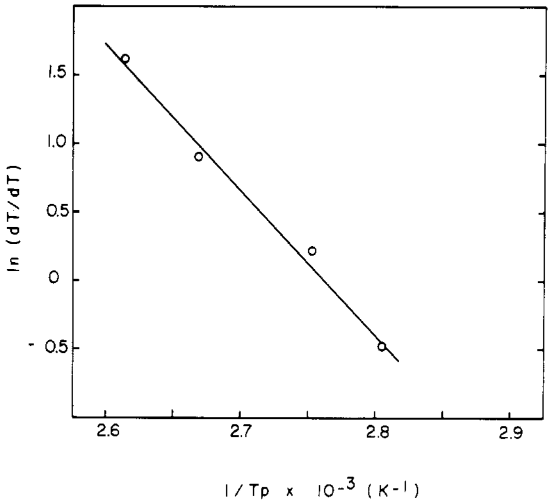

Figure 4. Relationship between ln [dT/dt] and 1/T for four different dynamic measurements (TRIM-MMA copolymerization in the presence of ethyl acetate; monomer:solvent = 30:70; the monomer mixture consisted of 80% TRIM and 20% MMA). Application of eq 9.

A typical dynamic DSC thermogram of a TRIM-MMA copolymerization (scanning rate = 2.5 °C/min) is shown in Figure 3. The dynamic thermogram is more pronounced than the isothermal one in Figure 1, particularly at the break point. The same observations that are made from the isothermal thermogram are also valid for the dynamic one. The heat of reaction of the homopolymer systems was about the same (134 (±10%) J/g), while the copolymer systems differed having H_t values of 154 (±10%) J/g and 163 (±10%) J/g for the different solvents

Table IV
Calculation of the Activation Energy According to Equation 9 for Two Homopolymerization Systems[a] and for Two Copolymerization Systems[b]

polymeriztn system	activation energy kcal/mol	activation energy kJ/mol
TRIM-TOL	20.4	83.8
TRIM-ETAC	19.7	82.3
TRIM-MMA-TOL	21.1	88.2
TRIM-MMA-ETAC	21.4	89.5

[a] 30% TRIM and 70% solvent (toluene or ethyl acetate). [b] 30% monomer mixture consisting of 80% TRIM and 20% MMA in 70% solvent (toluene or ethyl acetate).

toluene and ethyl acetate, respectively. No dependence between the heat of reaction and the heating rate was observed.

The thermograms obtained at various rates were analyzed by using the Kissinger method by the application of eq 9. Figure 4 shows a typical plot obtained from this method and in Table IV the activation energies for the four different systems investigated are shown. Linearization of the peak temperatures (T_p) also confirms the assumption that E is independent of the heating rate and that the reaction order is constant throughout the greater part of the polymerization and independent of the scanning rate used.

The value of the activation energy is about 20 kcal/mol, independent of the solvent used. The copolymerization of TRIM with MMA also shows approximately the same result. The result obtained is also in good agreement with the results obtained with isothermal measurements.

Comparison with NMR Investigations. The kinetic order of reaction, determined by NMR[4], for the homopolymerization in toluene and ethyl acetate varied between 1.4 in the beginning of the polymerization (conversion between 5% and 30%) to 1.0 at the end (conversion above 75%). The kinetic order of reaction obtained from isothermal DSC measurements was about 1.0 for the same systems.

The higher value obtained with NMR at the beginning of the polymerization may be caused by an increase in temperature in the NMR sample tube. Exothermically generated heat has to be distributed over the tube wall to the gas stream in the probe.

The rapid increase in the polymerization rate at the break point is due to gel formation (gel effect). Very little of the polymerization occurs in the solution.[4] Most of the reaction occurs at the surface of the framework via polymerization of pendant methacrylate groups with TRIM molecules from the bulk.[1]

The copolymerization experiments show lower reaction order than the homopolymerizations. This is because the incorporation of methyl methacrylate groups increases the mobility of the radical ends and therefore facilitates termination reactions.

Conclusion

The assumption that the activation energy and the kinetic order of reaction are independent of the conversion was confirmed by the obtained straight lines in the calculations. The activation energies were about the same for all four polymerization systems and independent of the method used. The kinetic order of reaction was about 1.0 for the homopolymerization systems investigated which shows that at constant temperature the polymerization was only controlled by the monomer concentration. These results clearly show that in spite of the fact that the polymerization occurs in a gel the diffusion of monomer into the reactive sites is rapid and sufficient.

The comparison of the break points observed in the DSC thermograms, both isothermal and dynamic, with previous observations[4] of the gel point shows that it is probable that the break point in the DSC thermograms occurs in connection with the formation of a gel.

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Registry No. TRIM, 3290-92-4; MMA, 80-62-6.

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