Study of post-gelation reaction by differential scanning calorimetry

Zoran S. Petrović* and Jaroslava Budinski-Simendić
Institute for Petrochemistry, Gas, Oil and Chemical Engineering, Faculty of Technology, Novi Sad, Yugoslavia

and Tatjana Malavašić
Chemical Institute Boris Kidrič, Ljubljana, Yugoslavia

and William J. MacKnight
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, USA

(Received 22 March 1989; revised 28 August 1989; accepted 3 October 1989)

Determination of conversion in the polycondensation of polyfunctional monomers above the gel point is complicated by insolubility of the polymer. The use of d.s.c. can overcome this difficulty if it affords sufficient accuracy. The aim of this work was to estimate the accuracy of the d.s.c. determination of conversion in the reaction of tris(4-isocyanatophenyl) thiophosphate and polypropyleneglycol of $MW = 1000$ model system. The calibration of the d.s.c. conversion values was carried out by titration of the isocyanate groups at different conversions in the pre-gel state. The results were then used to compare the conversion measured by d.s.c. with that from sol fraction measurements in the post-gel state. The relationship between the sol fraction and the degree of conversion for our system was obtained from cascade theory. Reasonable agreement between the d.s.c. and sol fraction methods was found below 90% conversion.

(Keywords: gelation; d.s.c.; model polyurethanes)

INTRODUCTION

The study of the gelation of polyfunctional monomers beyond the gel point is difficult because such materials are insoluble and not amenable to most of the standard techniques for measurement of conversion. In the case of a difunctional polyol and a triisocyanate, it is, in principle, possible to measure conversion beyond the gel point by infra-red red spectroscopy, following the absorption of the very strong isocyanate group at 2275–2240 cm^{-1}. However, experience shows that the reaction in the very thin film, suitable for infra-red, does not proceed in the same way as in bulk. Also, the process of sample preparation for i.r. measurements after gelation occurred, is extremely difficult and time consuming. With the development of modern high precision instrumentation, differential scanning calorimetry (d.s.c.) is offering new possibilities for studying the later stages of gelation. In order to examine the precision and applicability of the method to gelation study, a model system consisting of the polypropylene glycol (PPG), having $MW = 1000$, and tris(4-isocyanatophenyl) thiophosphate was reacted and the degree of conversion measured by d.s.c. and titration before the gel point, and by d.s.c. and sol fraction measurement after the gel point. Conversion beyond the gel point can be obtained from sol fraction measurements and gelation theories. Gelation theories can be divided into several groups. The first is the probability theory of Flory–Stockmayer[1], the second is cascade (or branching) theories[2]; the third, percolation theories[3] and the fourth, kinetics theories[4]. This fact alone indicates that there are still some unsolved problems and different approaches offer new insights into the phenomenon. One of the unsolved problems is associated with the assessment of the degree of intramolecular reactions[5]. However, if intramolecular reaction is present then the theories mentioned may be adapted to take approximate account of such reaction. The resulting approximations become less accurate, the greater the degree of intramolecular reaction. Experimentally, the degree of intramolecular reaction can be assessed by measuring the dependence of molecular weight on conversion. Intramolecular reactions increase conversion without increasing the molecular weight of the polymer. In order to study intramolecular reactions after the gel point one can compare the sol fraction from theory (for the ideal case without intramolecular reactions) with the experimental value at a given conversion. Thus, the precise degree of conversion is required. Conversion, p, from d.s.c. can be calculated directly by measuring the enthalpy of the unreacted part at a given time, H, and using the initial enthalpy H_0, according to the relationship:

$$p = (H_0 - H)/H_0 \qquad (1)$$

This equation is correct provided the reaction heat is independent of the substitution in the triisocyanate. If the reaction is slow then samples can be taken at regular times and simultaneous d.s.c. analysis and titration can

---

* To whom correspondence should be addressed at: Tehnološki Fakultet, 21000 Novi Sad, V. Vlahovića 2, Yugoslavia

0032-3861/90/081514-05

be carried out. In our case the system requires about 1 h for about 1.5% conversion near the gel point, at 25°C. This allows time for titration and d.s.c. measurements. D.s.c. must be carried quickly enough to completion, which is the biggest experimental problem (theoretically an isothermal reaction extends to infinity). The selected isothermal temperature in the d.s.c. was 120°C. At this temperature the reaction is completed in a reasonable time without significant side reactions. At higher temperatures the basic reaction is faster but the dissociation of the urethane bond is pronounced.

EXPERIMENTAL

Materials

Polypropylene glycol, PPG 1000, was purchased from Aldrich Chemical Co. The hydroxyl number was 112.8 mg KOH/g. Desmodur RF (designated as DRF) was obtained from Bayer Co. in the form of the 20% solution of triisocyanate in methylene chloride. The triisocyanate was obtained in very pure form by recrystallization from the native solution. The isocyanate content was equal to the theoretical value (27.1%).

Methods

The reaction between polyol and DRF was carried out in a 500 ml, three neck, round bottom flask, under dry nitrogen, equipped with a stirrer and $CaCl_2$ tube. The mixture was initially heated to 90°C to melt the triisocyanate and homogenize the mixture with stirring. The temperature was then lowered to 30°C. The samples were taken at different times for isocyanate content determination and d.s.c.. In order to increase the reaction rate the temperature was increased in steps of 5°C after each sample was taken for measurement. In the post-gel state the temperature was raised and held at about 90°C. This procedure allowed the measurements to be carried out in one day. Past the gel point, conversion was measured by measuring the sol fraction. Measurement of the sol content in the samples, treated with methanol to block free isocyanate groups, was carried out after extraction in toluene for 7 days. D.s.c. measurements were carried out using a Perkin–Elmer DSC-7 apparatus. NCO content was determined by titration of the excess dibutylamine with 1 N HCl, according to ASTM D 1638-74.

RESULTS AND DISCUSSION

The enthalpy of the reaction is directly proportional to the number of reacted isocyanate groups. Initially, samples were heated at 5°C/min from room temperature up to about 200°C. *Figure 1* displays a d.s.c. curve for one of the samples. The determination of the peak area under these conditions was not considered satisfactory, first because the reaction might not be complete, and second, at high temperatures (around 200°C), dissociation of the urethane bond or allophanate formation may take place. However, kinetics data obtained from the dynamic analysis allowed the construction of isothermal curves at several temperatures (*Figure 2*), from which the experimental conditions were established. After careful examination, isothermal heating at 120°C was employed. At this temperature isocyanate side reactions are minimized, the reaction rate is fast enough and the peak is well defined. A sample of about 20 mg was used. The samples were allowed a short time (about 1 min) to reach the preset instrument temperature of 120°C. Analysis time was limited to 40 min. Longer times would contribute to somewhat higher reaction enthalpies but it was assessed that the same error is made in measuring total and partial enthalpies so that such errors approximately cancel out. *Figure 3* illustrates the d.s.c. curves for two reaction times; the smaller peak corresponds to the longer reaction time. Because the initial enthalpy cannot be measured, it was assessed from a single measurement of the enthalpy at a given conversion, measured by titration of isocyanate groups, using equation (1). The correct measurement of the enthalpy requires precise measurement of the peak

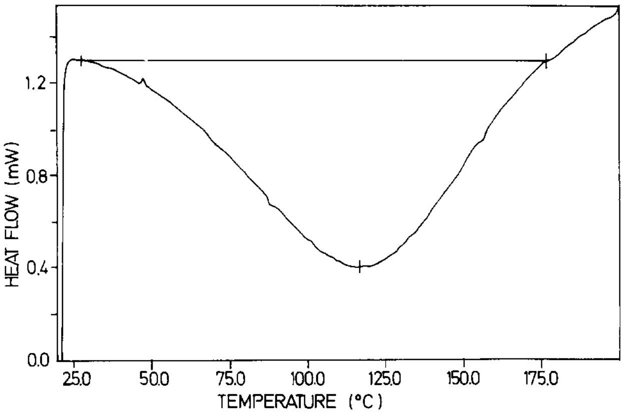

Figure 1 The course of the triisocyanate-polyol reaction, heating rate 10 K/min

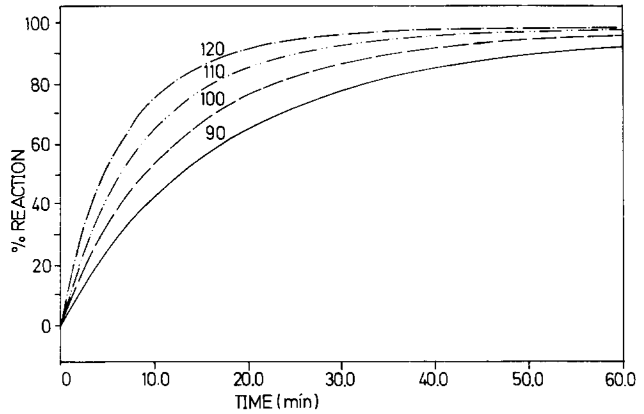

Figure 2 Degree of conversion vs. time for isothermal reactions at different temperatures calculated from the course of the reaction on *Figure 1*. ——, 90°C; — —, 100°C; — · · —, 110°C; — · —, 120°C

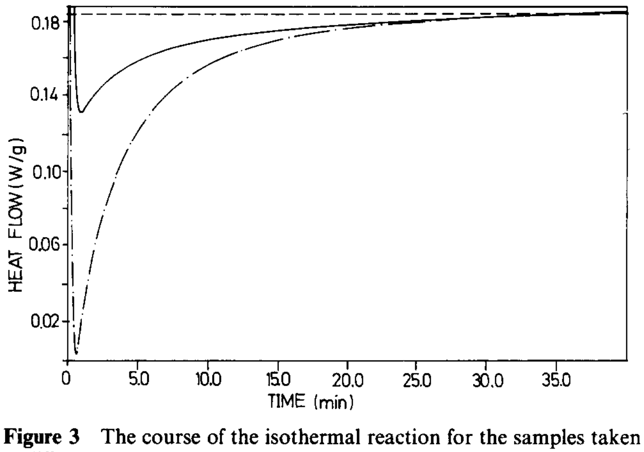

Figure 3 The course of the isothermal reaction for the samples taken at different reaction times and conversions, — · —, 43.3% of conversion; ——, 73.4% of conversion; ——, baseline

area, which depends on the accuracy of the base line. The horizontal base line extrapolated from complete conversion was considered to be the most appropriate. *Table 1* displays NCO contents at different reaction times, determined by titration, and corresponding enthalpies of reaction. Average values of the enthalpy of the 100% reacted system were found to be −102.6 J/g in the first series, −104.5 J/g in the second, −104.5 J/g in the third, −105.2 in the fourth, −106.2 in the fifth and −104.9 in the sixth. H_0 values were taken to be variable and the values for each series, obtained from the pre-gel measurements were taken for calculation in the post-gel state. Using the average value in each group as H_0 the conversion beyond the gel point could be calculated from the enthalpy, H, of the unreacted part at the given time. In order to assess the accuracy of the measured value beyond the gel point, an independent degree of conversion should be determined. This could be done by measuring the sol fraction in the sample. A brief outline of the method will be presented.

Gelation theories use complex mathematical expressions for the calculation of conversion from the sol fraction in the case of two or more component systems. The expression applicable to our system is developed here using the cascade theory of gelation[3,6–9]. Initial quantities required for the calculation of the conversion from the sol fraction, in the system of a triisocyanate and a diol are:

n_{I3}	molar fraction of the triisocyanate $[=N_I/(N_H+N_I)]$
M_{I3}	molecular weight of the triisocyanate
n_{H2}	molar fraction of the diol $[=N_H/(N_H+N_I)]$
M_{H2}	molecular weight (M_n) of the diol
r_H	initial molar ratio of [OH] to [NCO] groups $(=p_I/p_H=1/r_I)$
p_I	the conversion of isocyanate groups
p_H	the conversion of hydroxyl groups

The probability generating function (PGF) for the f-functional monomer in the zeroth generation (root) is:

$$F_0(z)=(1-p+pz)^f \quad (2)$$

where z is a dummy variable, used only to facilitate the mathematical operations and has no physical meaning.

PGF for the number of bonds issuing from the diol unit in the zeroth generation, $F_{0H}(z)$, is:

$$F_{0H}(z_I)=(1-p_H+p_Hz_I)^2 \quad (3)$$

while PGF for the number of bonds issuing from the triisocyanate in the zeroth generation, F_{0I}, is:

$$F_{0I}(z_H)=(1-p_I+p_Iz_H)^3 \quad (4)$$

In order to calculate the relationship between sol fraction, w_s, and conversion it is necessary to calculate the extinction probabilities. By definition the extinction probability of a bond is the probability that the bond

Table 1 Relationship between conversion from the isocyanate content, p(NCO), and enthalpies of isocyanate/polyol reaction; x = mean, s = standard deviation

Reaction time, min	wt% NCO	p (NCO)[a]	H J/g	H_0 J/g
Run 1 (initial wt% NCO = 6.45)				
35	4.14	35.8	−59.8	− 93.1
151	3.36	47.9	−57.1	−109.6
196	3.15	51.2	−51.3	−105.1
				$x=-102.6$ $s=8.53$
Run 2 (initial wt% NCO = 6.45)				
30	2.90	55.0	−49.9	−110.9
80	2.65	58.9	−43.1	−104.9
130	2.36	63.4	−35.8	− 97.8
				$x=-104.5$ $s=6.56$
Run 3 (initial wt% NCO = 6.45)				
30	3.40	47.3	−55.4	−105.1
80	2.84	56.0	−50.6	−115.0
190	2.61	59.5	−38.7	− 95.6
230	2.35	63.5	−37.2	−102.2
				$x=-104.5$ $s=8.06$
Run 4 (initial wt% NCO = 6.45)				
35	3.18	50.7	−53.6	−108.7
85	3.06	52.6	−48.2	−101.7
				$x=-105.2$ $s=4.95$
Run 5 (initial wt% NCO = 6.46)				
60	3.66	43.3	−57.4	−101.2
105	3.33	48.5	−48.5	−112.4
155	3.16	51.1	−53.5	−109.4
205	2.97	54.0	−43.9	− 95.4
255	1.71	73.5	−29.9	−112.8
				$x=-106.2$ $s=7.65$
Run 6 (initial wt% NCO = 6.45)				
35	4.55	29.5	−74.6	−105.8
80	3.94	38.9	−67.4	−110.3
130	3.66	43.3	−56.2	− 99.1
180	3.16	51.0	−52.5	−107.1
225	3.03	53.0	−48.1	−102.3
				$x=-104.9$ $s=4.34$
				overall $x=-104.8$ $s=6.12$

[a] Measured by titration

will not continue into an infinite chain. In the case of the two component system such as ours, there are two extinction probabilities v_H and v_I.

The extinction probability is equal to the first generation PGF, which is defined as:

$$F_1(z) = [dF_0(z)/dz]/[dF_0(z)/dz]_{z=1} = F'_0/F'_0(1) \quad (5)$$

and

$$v_H = F_{1H}(v_I) \quad (6)$$

$$v_I = F_{1I}(v_H) \quad (7)$$

The calculation of v_H from F_{1H} (and replacing z_I with v_I) and v_I from F_{1I}, gives:

$$v_H = (1 - p_H + p_H v_I) \quad (8)$$

$$v_I = (1 - p_I + p_I v_H)^2 \quad (9)$$

By combining equations (8) and (9) expressions (10) and (11) are obtained:

$$1 - v_I = (2p_I p_H - 1)/(p_I^2 p_H^2) \quad (10)$$

$$1 - v_H = (2p_I p_H - 1)/(p_I^2 p_H) \quad (11)$$

The calculation of the sol fraction is obtained from the condition that:

$$w_s = m_{H2} F_{0H}(z_I = v_I) + m_{I3} F_{0I}(z = v_H) \quad (12)$$

where m_{H2} and m_{I3} are weight fractions of diol and triisocyanate, respectively.

In our case

$$m_{H2} = n_{H2} M_{H2}/\bar{M} \quad (13)$$

and

$$m_{I3} = n_{I3} M_{I3}/\bar{M} \quad (14)$$

while

$$\bar{M} = n_{H2} M_{H2} + n_{I3} M_{I3} \quad (15)$$

The probability generation functions F_{0H} and F_{0I} are in our case given by:

$$F_{0H}(z_I = v_I) = (1 - p_H + p_H v_I)^2 \quad (16)$$

$$F_{0I}(z_H = v_H) = (1 - p_I + p_I v_H)^3 \quad (17)$$

Thus, the final expression relating sol fraction, w_s, and conversion of isocyanate groups, p_I, is:

$$w_s = m_{H2} x^2 + m_{I3} y^3 \quad (18)$$

where

$$x = [1 - p_H(1 - v_I)] \quad (19)$$

and

$$y = [1 - p_I(1 - v_H)] \quad (20)$$

Thus, the calculation of the sol fraction requires the knowledge of p_I (measured) and $p_H = p_I r_I$, or vice versa. The values of $(1 - v_I)$ and $(1 - v_H)$ are given by expressions (10) and (11). Since $r = 1$ in the stoichiometric case, $p_I = p_H$. A numerical solution of equation (18) can be carried out relatively easily and with high precision. For the stoichiometric case ([OH]/[NCO] = 1), where the triisocyanate molecular weight is 465 and the diol M_n = 1000, $m_{H2} = 0.7634$ and $m_{I3} = 0.2366$ (i.e. $m_{H2} + m_{I3} = 1$). *Table 2* illustrates the dependence of the amount of sol

Table 2 Theoretical dependence of sol fraction on conversion for the system DRF/PPG1000 assuming no intramolecular reactions

p	0.7071	0.75	0.8	0.85	0.9	0.95
w_s	0	0.589	0.199	0.071	0.020	0.003

Table 3 Conversions in the triisocyanate/polyol reaction calculated from d.s.c. and sol fraction measurements; x = mean, s = standard deviation

Reaction time, min	H J/g	p (d.s.c.) %	w_s	p (sol) %	Δp %
Run 1					
60	−29.2	71.5	0.413	76.0	−4.5
256	−19.0	81.8	0.079	84.5	−2.7
1200 (next day)	− 1.9	98.2	0.079	89.4	8.8
Run 2					
60	−28.3	72.9	0.363	76.7	−3.8
120	−17.3	83.4	0.117	82.7	0.7
1320 (next day)	− 6.7	93.6	0.047	86.8	6.8
Run 3					
330	−20.8	80.1	0.318	77.5	2.6
370	−19.6	81.2	0.193	80.2	1.0
Run 4					
292	−23.3	77.9	0.377	76.5	1.4
347	−15.3	85.5	0.188	80.3	5.2
1440 (next day)	− 7.3	93.1	0.032	88.3	4.8
Run 5					
360	−26.6	75.0	0.414	76.0	−1.0
405	−26.1	75.4	0.266	78.5	−3.1
450	−22.0	79.3	0.186	80.4	−1.1
1800 (next day)	−15.0	85.9	0.041	87.3	−1.4
Run 6					
285	−34.0	67.6	0.578	74.1	−6.5
330	−31.4	70.1	0.365	76.7	−6.6
380	−23.2	77.9	0.189	80.3	−2.4
430	−17.9	82.9	0.120	82.6	0.3
				overall $x = -0.08$	$s = 4.29$

fraction on conversion for the system DRF/PPG1000. Roughly, w_s decreases with the third power of conversion. Calculated conversions from d.s.c. and sol fraction are given in *Table 3*.

The average value of the initial reaction enthalpy, H_0, was found to be -104.8 J/g with the relatively large standard deviation $s = 6.12\%$. The difference between the results of the conversion measured by d.s.c. and sol fraction method, Δp, expressed in percentages, varies from 8.8% to -6.6%, but most values are less than 3%. These results also show that conversion above 90% is difficult to measure because of very low enthalpies of reaction and small sol fractions, resulting in large difference in conversion. If a value of 8.8% from the first run is excluded mean difference would be -0.57% and $s = 3.8\%$. When all three values measured above 90% conversion are excluded mean difference becomes -1.4% and $s = 3.2\%$.

The small mean value of the difference is obtained on account of the cancellation of positive and negative values. Thus standard deviation is a more important measure of measurement errors. However, the value of $s = 3.2\%$ shows that the precision of the d.s.c. method is close to that of titration and sol measurement. Generally, conversions obtained by d.s.c. are lower than those from the sol fraction measurement although the difference is very small. If intramolecular reactions take place then for the same conversion higher sol content would be expected compared to the ideal case, or assuming no intramolecular reactions lower conversion will be obtained. In a separate study of gelation of the same system it was found that the measured critical conversion is higher for about 1–2% than theoretical. An error in the conversion measurement greater than 1% is not satisfactory for precise studies of intramolecular reaction but in other experiments an error of a few percent may be tolerated. Errors may also arise from the incorrect titration of isocyanate groups, especially when only a single measurement of the conversion is carried out. Thus, the precision of the d.s.c. measurements may be considered to be of the same order as that from the sol fraction method and close to that from titration.

CONCLUSIONS

The possibility of using d.s.c. for assessing conversion in a triisocyanate–macrodiol reaction in the gel state was examined. D.s.c. isothermal measurements were carried out at 120°C. In spite of some arbitrariness of the choice of the base line, the method gave reasonable precision. The precision can be improved by taking several measurements at one degree of conversion and using longer experimental times (i.e. lower reaction temperatures). The method is very rapid and allows the fast estimation of conversion in the gel state. The average value of the total enthalpy of the reaction was found to be 104.8 J/g. The differences in conversion measured by d.s.c. and sol fraction varied between less than 1% to 9%. Poor agreement between d.s.c. and the sol measurement method above 90% of conversion may be caused by the imprecision of the latter, due to the small amounts of the sol fraction (below 2%) and thus a high relative error.

ACKNOWLEDGEMENTS

This work has been supported by the Scientific Fund of Vojvodina and NSF(USA) grant JFP537. We are indebted to K. Dušek and M. Ilavský of Czecoslovak Academy of Sciences for helpful suggestions.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, p. 348
2 Gordon, M. *Proc. Roy. Soc. (London)* 1962, **A268**, 240
3 Staufer, D., Coniglio, A. and Adam, M. *Adv. Polym. Sci.* 1982, **44**, 103
4 Kuchanov, S. I. 'Metody Kineticheskih Raschetov v Himii Polimerov', Himiya, Moskva (1978)
5 Stepto, R. F. T. in 'Development in Polymerization—3' (Ed. R. N. Haward), Applied Science, London, 1982, p. 81
6 Dušek, K. *Adv. Polym. Sci.* 1986, **78**, 1
7 Dušek, K. *Rubber Chem. Technol.* 1982, **55**, 1
8 Dušek, K. and Ilavský, M. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1323
9 Ilavský, M. and Dušek, K. *Polymer* 1983, **24**, 981