

A Facile Method for the Study of Slow Physical and Chemical Processes in Polymeric Systems

ROGER LUNDGREN and ROLAND SANDÉN, *National Defence Research Institute, P.O. Box 551, S-14725 Tumba, Sweden*, and
ANN-CHRISTINE ALBERTSSON, *Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden*

Synopsis

A method is described for continuously following a long-duration process in a complex polymeric system by isothermal calorimetry. Computerized models for slow physical or chemical processes have been applied to calorimetric runs under different conditions and these have given information in the form of thermodynamic and kinetic data. The method also gives a means of determining the relationship between molecular weight and functionality for one of the polymers used, the order of reaction, and the degree of conversion before the start of the measurements. An example is given of a kinetic study of the reaction of hydroxyl-terminated polybutadiene with two different diisocyanates. The temperature dependence of the formation of urethanes, the rate constants, and the degree of conversion before the start of the measurements were determined as well as the heat of reaction for the formation of urethanes using hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) as curing agents. The results have been compared with other kinetic studies of these systems.

INTRODUCTION

It is very important in polymer technology to be able to predict the long-term properties of new materials. Polymers are often tailor-made for new applications where it is essential that the very slow processes which may occur in the new material, chemical and physical aging, post-curing etc., are fully understood.

The methods so far used are not reliable and are time-consuming. They are generally based on some kind of accelerated exposure of the material. This means, in a complex system, that different reactions are speeded up to different degrees and that the results are therefore difficult to relate to normal conditions.

These processes have in common that they either liberate or absorb heat. The thermal power, $P = dQ/dt$, is proportional to the rate of the process and the calorimeter is the general analytical tool for measuring the thermal power. When a polymeric material is studied by isothermal calorimetry, a continuous reading of the total heat absorbed or liberated can be obtained. This embraces both chemical and physical processes at a given temperature and in a given environment. If it is possible in a complex material to separate one process from other simultaneous processes, that process may be followed continuously. If the sensitivity of the calorimeter is sufficient, even slow processes in

relative small samples can be studied under normal conditions. This is accomplished by combining microcalorimetric measurements with computerized models, taking into consideration the processes involved. Results obtained in this way provide a useful complement to those from methods hitherto used for predicting long-term properties of polymeric materials.

The purpose of our study was to obtain quantitative data for a certain reaction and to eliminate other simultaneous reactions. In this paper, a method is described in which kinetic models have been computerized so that the initial heat, which is generally not obtained with isothermal calorimetry, can be determined, and where disturbances from other simultaneous processes are eliminated.

Using the method, the kinetics of the reaction between a hydroxyl-terminated polybutadiene (HTPB) and two curing agents, isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI), were studied. The method was used to handle the post-curing effect in a new model and describing the autoxidation of the cured polymer.

EXPERIMENTAL

Materials

The polymer used was hydroxyl-terminated polybutadiene R-45HT from ARCO, USA ($M_n = 2700$, functionality ≈ 2.3) with 2 pph 2,2'-methylenebis(4-methyl-6-tertiary-butylphenol) (BKF) from Bayer AG, West Germany, added as antioxidant. Isophorone diisocyanate (IPDI) from Hüls AG, West Germany, and hexamethylene diisocyanate (HDI) from Bayer AG, West Germany, were used as curing agents.

Calorimetry

Calorimetric measurements were performed with a multichannel microcalorimeter, LKB 2277 Thermal Activity Monitor, equipped with four calorimetric ampoule units permitting four samples to be measured simultaneously. The instrument has been described by Suurkuusk and Wadsö.¹ The calorimeter is isothermal and of the twin heat conduction type, immersed in a water thermostat, kept within $\pm 0.0001^\circ\text{C}$ from the set measurement temperature. Measurements were performed at 37, 50, 60, and 70°C and the absolute temperature was determined to within $\pm 0.02^\circ\text{C}$. The measurement vessels (2.5 mL disposable glass ampoules) were charged with 2 mL of the polymer. The reference vessel was an empty glass ampoule.

The power signal was recorded on a potentiometric recorder (LKB 2210-022), having a sensitivity of $\pm 0.2 \mu\text{W}$ and a baseline stability over 24 h of $\pm 0.2 \mu\text{W}$.

The ampoules were equilibrated for 15–20 min at the measurement temperature before they were placed in the measuring position. Depending on the experiment, a true power signal was received after a further 0.5–3 h.

Procedures

The heat of reaction for the formation of urethanes was determined in air at 37°C with IPDI and HDI as curing agents. The polymer (HTPB), with

BKF as antioxidant, was mixed with the curing agent for 2 min at 22°C and then directly measured.

The temperature-dependence measurements of the curing reaction were carried out in air at 37, 50, 60, and 70°C (system IPDI/HTPB + BKF). Before the start of the measurements the components were mixed for 15 min at 50°C and then kept for 2.1 h at 22°C.

Calculations

The reaction between two substances A and B gives the product C according to



where A , B , and C express the concentrations of each substance in the sample (mol/g).

If $A \neq B$, t = time and k is the rate constant, and, if it is assumed that this is a second order reaction as is appropriate in the present case,²⁻⁴ we obtain the following model:

$$\ln \frac{A - C}{B - C} = (A - B)k \cdot t - \ln \frac{B}{A} \quad (2)$$

In the present case the formation of C is an exothermal reaction. The microcalorimetric measurements give the power signal P (J/s) as a function of time t (s). $Q(t)$ is the heat liberated (J/g), and this can be calculated according to

$$Q(t) = Q_0 + \int_{t_1}^{t_\infty} P dt \quad (3)$$

where $Q_0 = \int_{t_0}^{t_1} P dt$ is the initial heat, which is not obtained in the measurements, and $\int_{t_1}^{t_\infty} P dt$ is the measured heat.

Equation (2) contains the unknowns C and k , but the crosslinked product (C) is given by

$$C = Q(t)/\Delta H \quad (\text{mol/g}), \quad (4)$$

where ΔH is the enthalpy of reaction (J/mol). The initial concentrations of A and B are known and can be written as

$$A = x_A/M_A \quad (\text{mol/g}) \quad (5)$$

and

$$B = x_B/M_B = z(1 - x_A)/M_A \quad (\text{mol/g}) \quad (6)$$

where M = molecular weight/binding site, $z = M_A/M_B$, the ratio of molecular weight/binding site, m = weight of reactant, and $x_A = m_A/m_{\text{tot}}$, the fraction of weight A where $m_{\text{tot}} = m_A + m_B$.

Equation (2) can therefore be rewritten in the form

$$\ln \frac{x_A/m_A - Q(t)/\Delta H}{z(1-x_A)/M_A - Q(t)/\Delta H} = \frac{1}{M_A} [x_A - z(1-x_A)] k \cdot t - \ln \frac{z(1-x_A)}{x_A} \quad (7)$$

Equation (7) has three unknown quantities, k , $Q(t)_0$, and ΔH .

Equation (2) as (7) can be transformed to give respectively the following equations:

$$C = \frac{A(e^{(A-B) \cdot k \cdot t} - 1)}{Ae^{(A-B) \cdot k \cdot t}/B - 1} \quad (\text{mol/g}) \quad (8)$$

as

$$\frac{Q(t)}{\Delta H} = \frac{(x_A/M_A)(e^{Kt} - 1)}{x_A e^{Kt}/z(1-x_A) - 1} \quad (\text{mol/g}) \quad (9)$$

where $K = (1/M_A)[x_A - z(1-x_A)]k$.

Equation (7) can be solved if x_A , M_A , M_B , and $P = f(t)$ are known. In a computerized model where a sufficiently large ΔH interval is scanned step by step, an initial Q_0 value is assumed for each value of ΔH . By iterative substitution using the calculated k from eq. (7) a new Q_0 is calculated according to

$$Q_0 = \Delta H \frac{(x_A/M_A)(e^{Kt_1} - 1)}{x_A e^{Kt_1}/z(1-x_A) - 1} \quad (\text{J/g}) \quad (10)$$

where t_1 is the time of the first measurement. This procedure is repeated until the Q_0 value converges. If the model used [eq. (7)] is correct, the simulation curve for a given ΔH will comply with the measurement curve.

RESULTS AND DISCUSSION

The reaction conditions were determined by choosing temperature, environment, and additives so that the desired reaction predominated during the measurement period. Still there are disturbances in the state of a residual contribution of power from a physical or chemical process. These disturbances are permissible as long as it is possible to handle them in the calculations. During the measurement, liberated or absorbed heat is continuously recorded as thermal power ($P = dQ/dt$) as a function of time. This is integrated to heat liberated or heat absorbed ($dQ = P dt$), which in turn is converted to concentrations appropriate to the model used. The relevant order of reaction (in this case, second order) is used as a model and the calculated "thermal power vs. time graph" is compared with the measurement graph.

Using isothermal calorimetry, it is possible to measure the heat absorbed or liberated from almost any physical and chemical process in a material. It should be possible to study even a slow process like autoxidation or aging.

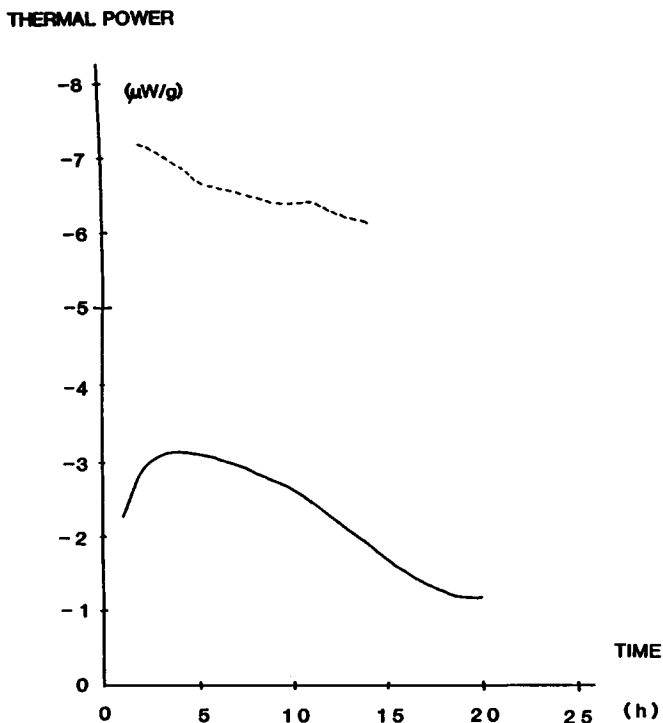


Fig. 1. The thermal power ($P = dQ/dt$) of pure hydroxyl-terminated polybutadiene at 40°C as a function of time in air (---) and in nitrogen (—).

Figure 1 shows the thermal power of pure hydroxyl-terminated polybutadiene at 40°C as a function of time in air and in a nitrogen atmosphere. The thermal power signal was significantly higher in the test (about $-7 \mu\text{W/g}$) than in the nitrogen test (about $-2 \mu\text{W/g}$).

Figure 2 shows the thermal power of hydroxyl-terminated polybutadiene with the antioxidant 2,2'-methylene-bis(4-methyl-6-tertiary-butylphenol) at 40°C as a function of time in air and in a nitrogen atmosphere. The power signals in tests with polymer plus antioxidant were the same within the limits of experimental accuracy for all the variables. The power is between -0.2 and $-0.4 \mu\text{W/g}$, which makes it lower by a factor of almost 10 than for the polymer alone (cf. Fig. 1).

Figure 3 shows the thermal power of the antioxidant 2,2'-methylene-bis(4-methyl-6-tertiary-butylphenol) alone at 40°C as a function of time in air and in nitrogen. The antioxidant agent itself has a power signal less than the error (Fig. 3). The results in Figures 1, 2, and 3 show that the pure polymer is oxidized in air, but that the oxidation is prevented by the addition of antioxidant.

Compared with earlier methods, e.g., C^{14} -labeling techniques,⁵ there was no need for special preparation of the polymer to study the influence of antioxidant. The behavior of polymer with and without antioxidant in an atmosphere of air was also compared at 70°C for 168 h. The curves obtained over 20 h are shown in Figure 4. Obviously most of the oxygen in the sealed

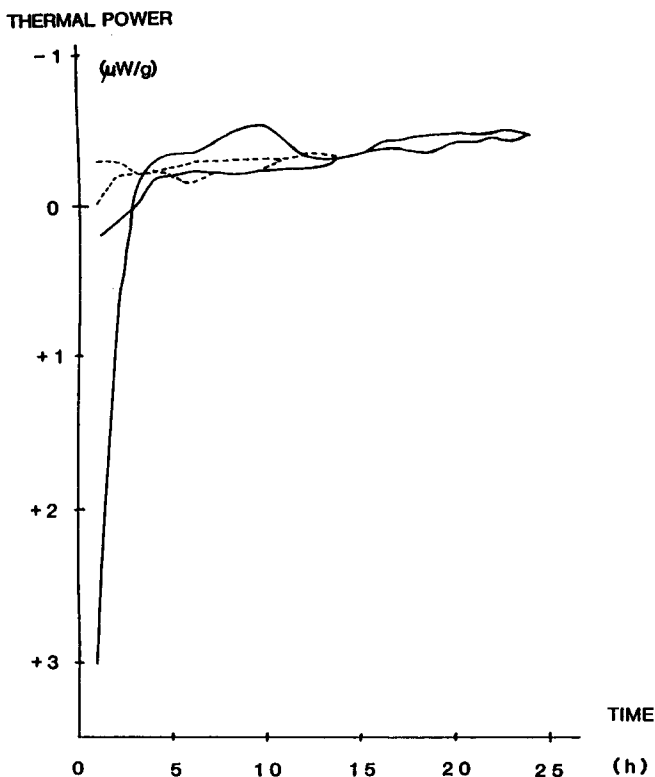


Fig. 2. The thermal power ($P = dQ/dt$) of hydroxyl-terminated polybutadiene with 2 pph of 2,2'-methylene-bis(4-methyl-6-tertiary-butylphenol) at 40°C as a function of time in air (---) and in nitrogen (—).

ampoule is consumed after 8 h with the pure polymer, but the thermal power liberated from the sample to which antioxidant was added shows a slight decrease. At 70°C, however, both samples show a residual contribution from a physical or chemical process.

The main purpose was, however, not only to study the oxidation or aging processes in the polymer but also to test a specific model (in this case of a curing or postcuring reaction) using calorimetric data. To test the model the measurements were started first after 2.1 h throughout the temperature dependence measurements. The "post-curing reaction" was followed for 168 h, and the conversion before start of the measurements were determined. In the reaction of the model, an important aspect was how to know and handle the influence of the slow processes incorporated in the systems used.

In the model used, it is possible to eliminate these disturbances due to slow processes by a subtractive method. The method is used throughout the temperature dependence calculations (Table I), i.e., in each series (temperature), but not in the calculations of the heat of reaction (Table II) since the samples were directly measured at 37°C, which means that the using reaction predominates. The disturbances increase with increasing temperature. The largest corrected for is at 70°C, where the amount is $-11 \mu\text{W/g}$ from 1 h decreasing to $-3 \mu\text{W/g}$ after 168 h.

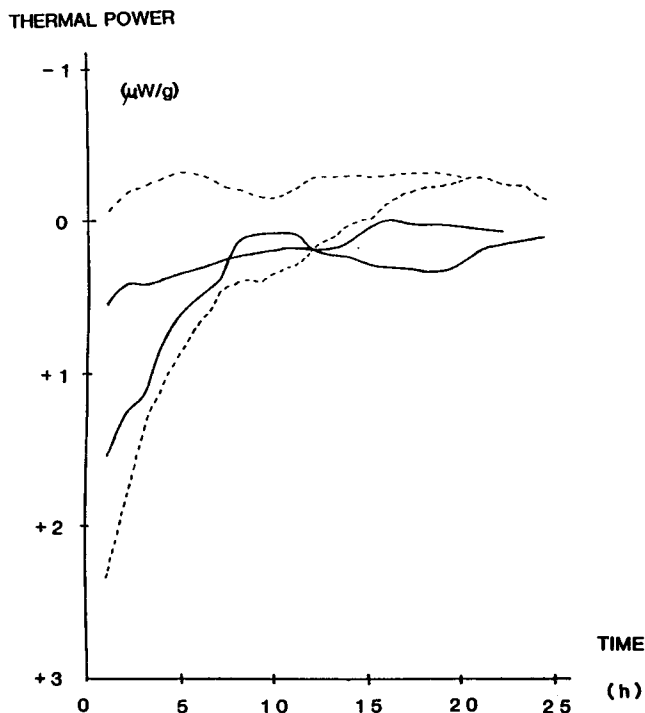


Fig. 3. The thermal power ($P = dQ/dt$) of 2,2'-methylene-bis(4-methyl-6-tertiary-butylphenol) at 40°C as a function of time in air (---) and in nitrogen (—).

In the tables STD(LOG) is the standard deviation calculated for the graph adjusted by the least squares method. STD(P) is the statistical sum of the errors between measured and calculated thermal power at each measuring point. Q_0 is the calculated initial heat and k is the rate constant of the reaction. The inverted expression $\ln(A/B)$ from eq. (2) is the ratio between the concentrations of curing agent (A) and polymer (B). For further information, see the Calculation section.

The temperature-dependence measurements of the curing reaction were carried out in air at 37, 50, 60, and 70°C (system IPDI/HTPB + BKF). The model calculation yields are compiled in Table I.

The value of Arrhenius activation energy, $E_A = 42$ kJ/mol (Fig. 5) agrees well with earlier experiments on the system IPDI/HTPB.²⁻⁴ It was also found by comparison of the heats of reaction under the conditions described (ΔH_{PUR} is known) that the degree of conversion before the start of the measurements was approximately 40%. The rate of the reaction also decreases depending on the degree of curing.

Figure 6 shows the curing reaction (thermal power as a function of time) of the polymer (HTPB) with the curing agent (IPDI) at 37°C over a period of 150 h, and Figure 7 shows the same reaction at 50°C. The standard deviations of the measured from the simulation curves are very small [see STD(LOG) and STD(P) in Table I], and the curves are visually very similar.

The determination of the heat of the formation of urethanes (ΔH_{PUR}) was carried out in air at 37°C with isophorone diisocyanate (IPDI) and hexam-

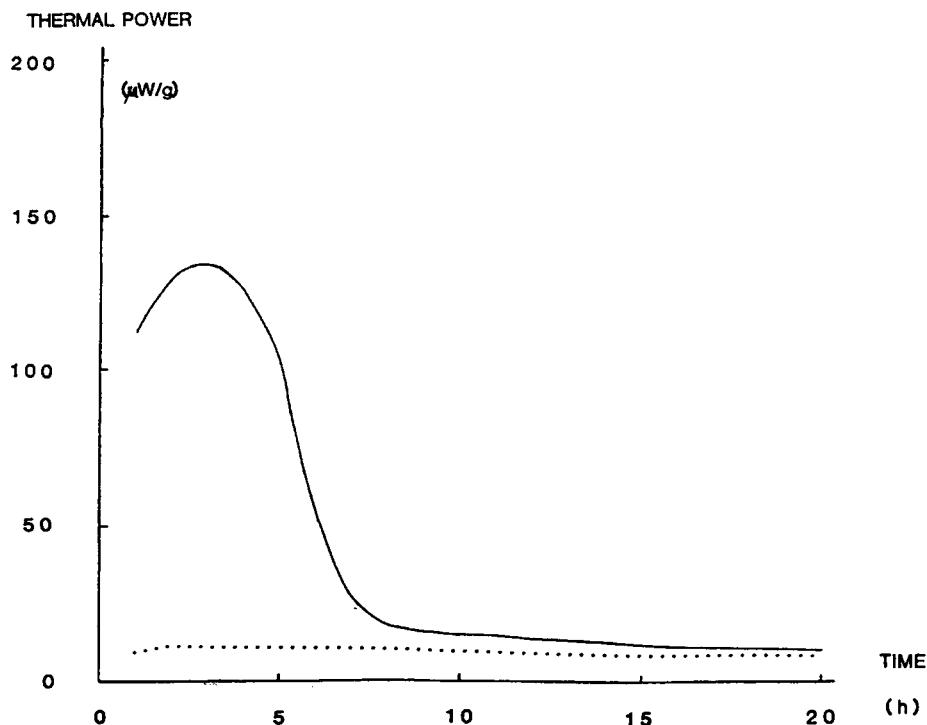


Fig. 4. The thermal power ($P = dQ/dt$) of hydroxyl-terminated polybutadiene in the presence (\cdots) and the absence (—) of 2,2'-methylene-bis(4-methyl-6-tertiary-butylphenol) at 70°C as a function of time.

TABLE I
Temperature Dependence of the Formation of Urethanes

System	Temp (°C)	STD(LOG) ($\times 10^{-4}$)	STD(P) ($\mu\text{W/g}$)	ΔH (kJ/mol)	Q_0 (J/g)	$\ln(A/B)$	$\ln(A/B)$ calculated	k g/(s mol)
IPDI/HTPB + BKF	37	0.017	2.4	46	2.9	0.0763	0.0763	0.029
	50	0.165	6.6	52	7.5	0.0763	0.0763	0.076
	60	0.336	5.8	36	5.8	0.0763	0.0764	0.088
	70	1.34	4.9	47	17.7	0.0763	0.0762	0.152

TABLE II
The Heat of Reaction for the Formation of Urethanes

System	Temp (°C)	STD(LOG) ($\times 10^{-4}$)	STD(P) ($\mu\text{W/g}$)	ΔH_{PUR} (kJ/mol)	Q_0 (J/g)	$\ln(A/B)$	$\ln(A/B)$ calculated	k g/(s mol)
IPDI/HTPB + BKF	37	7.82	15.3	78	7.3	0.0484	0.0476	0.051
	37	11.0	18.3	78	7.2	0.0484	0.0473	0.050
HDI/HTPB + BKF	37	6.23	23.4	89	10.3	0.0444	0.0450	0.056
	37	2.57	11.8	93	27.4	0.0444	0.0446	0.065

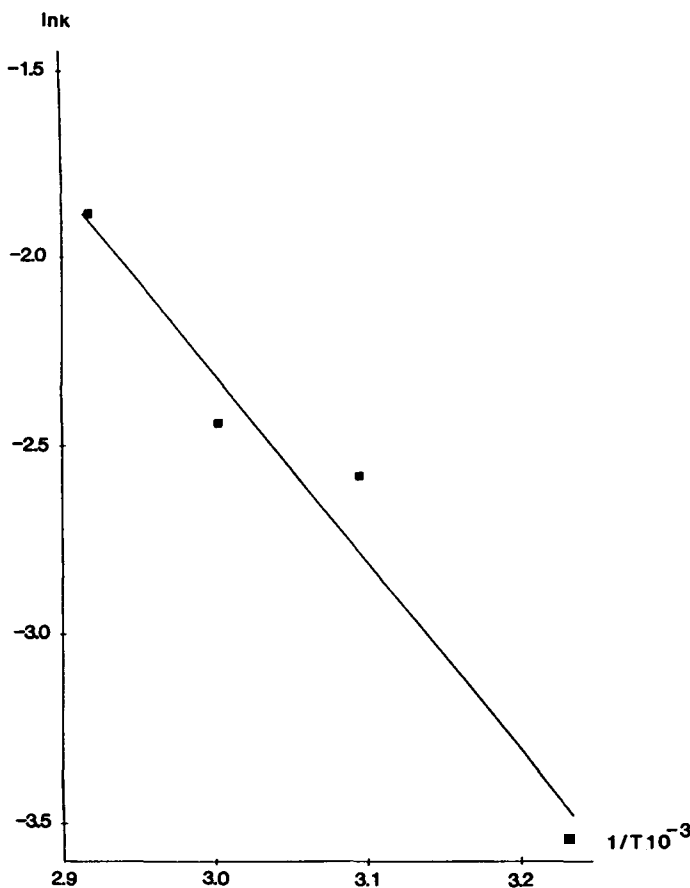


Fig. 5. Arrhenius plot (37, 50, 60, and 70°C) of the curing reaction of hydroxyl-terminated polybutadiene with isophorone diisocyanate. $E_A = 42$ kJ/mol.

ethylene diisocyanate (HDI) as curing agents. The model calculation yields are compiled in Table II.

The mean value of the results shows an enthalpy of reaction of approximately 84 kJ/mol which accords with the value given by others,⁶ as do also the rate constants of the two systems.²⁻⁴

The difference under the same conditions between the rate constants of the reaction in the two systems used under the same conditions is probably due to a difference between the reactivities of the isocyanate groups in the IPDI molecule which must be related to steric and inductive effects. The isocyanate group located on the primary carbon is more reactive and more similar to the groups in the HDI molecule. The calculated ratios of polymer and curing agent also agree well with the true ratios.

Obviously, with all other parameters known (including k and ΔH) the ratio between the molecular weight and functionality can be determined (vary z by varying M_B). It is also evident that different models of order of reactions can be tested, and the right one is established when the model data accord with the experimental values.

THERMAL POWER

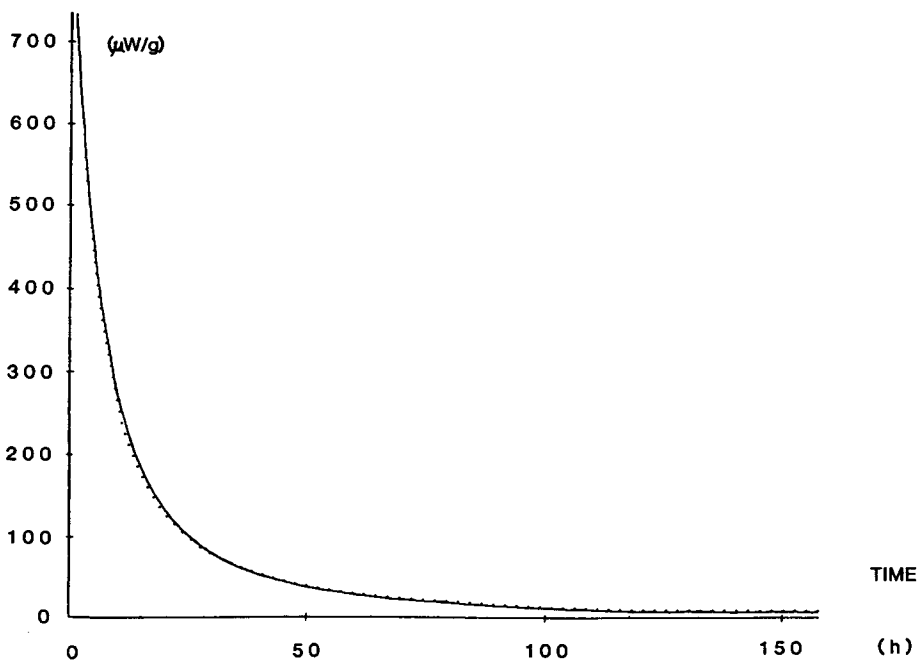


Fig. 6. The thermal power ($P = dQ/dt$) during curing of hydroxyl-terminated polybutadiene with isophorone diisocyanate at 37°C measured (···) and calculated (—). The start of the measurements (zero time) was 2.35 h after mixing.

THERMAL POWER

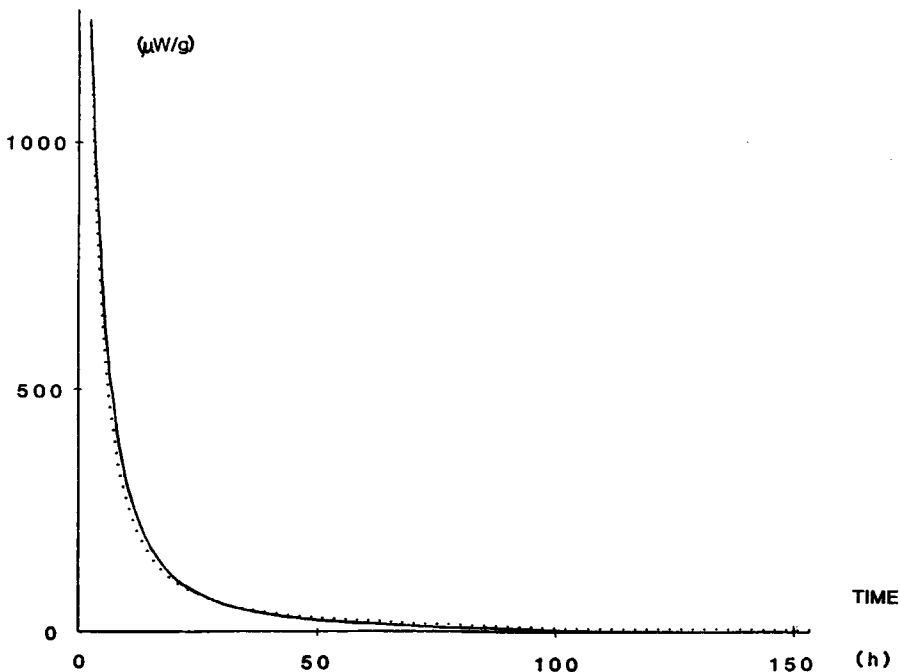


Fig. 7. The thermal power ($P = dQ/dt$) during curing of hydroxyl-terminated polybutadiene with isophorone diisocyanate at 50°C measured (···) and calculated (—). The start of the measurements (zero time) was 2.35 h after mixing.

CONCLUSIONS

The microcalorimeter combined with computerized models can be used not only for obtaining thermal data but also for other relevant data. The extremely high sensitivity of the instrument opens up a new possibility for the study of slow physical and chemical processes in polymer systems without special preparation of the polymer. Post-curing and the autooxidation of HTPB in air can be studied as well as the beneficial effect of the antioxidant BKF.

References

1. J. Suurkuusk and I. Wadsö, *Chemica Scripta*, **20**, 155 (1982).
2. Y.-G. Cheun, J.-K. Kim, D.-S. Ham, and J.-W. Lee, *Polymer (Korea)*, **9**, 2 (1985).
3. F. M. B. Coutinko, L. C. Rezende, and R. Quijada, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 3021 (1986).
4. R. Y. Yee and A. Adicoff, *J. Appl. Polym. Sci.*, **20**, 1117 (1976).
5. A.-C. Albertsson and Z. G. Banhidi, *J. Appl. Polym. Sci.*, **25**, 1655 (1980).
6. R. E. Welte, *J. Cell. Plast.*, (Sept.), 351 (1984).

Received November 16, 1987

Accepted February 15, 1988