Kinetics of Sulfur Vulcanization of 1,4-*cis*-Polyisoprene by Differential Scanning Calorimetry

N. N. Kolesnikova, O. A. Ostroukhova, A. A. Popov

N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciencis, Moscow 119334, Russia

ABSTRACT: The vulcanization of 1,4-*cis*-polyisoprene was studied by differential scanning calorimetry under isothermal and nonisothermal conditions. On the basis of thermal characteristics obtained, the kinetic parameters of crosslinking (the induction period, maximum rate, and effective energy of activation) were determined. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 754–757, 2007

Key words: differential scanning calorimetry; kinetics; vulcanization; polyisoprene

INTRODUCTION

As distinct from the conventional methods of studying the vulcanization of rubbers via determining the relationships between the kinetics and variable parameters that depend on a set of chemical reactions associated with crosslinking of macromolecules, DSC makes it possible to observe the process in progress by measuring its heat effects.

According to the data published, DSC is used in studies on the reactions of low molecular weight bi- and polyfunctional compounds that yield crosslinked polymer structures.[1–3] Data on using DSC in studies on the vulcanization of unsaturated rubbers are reported in few works.[4–5]

The application of DSC for quantitative measurements relies on the fact that the heat released while a sample is heated in a calorimeter is an indication of the course of the reaction (on condition that the sample mass remains unchanged during the experiment).[6] The experimental curves show the temperature or time dependences of the heat flow (dH/dt). The measurable parameters are the heat flow, i.e., the heat released per unit time (the DSC isotherm ordinate) and the amount of heat released (ΔH).

The DSC principal assumption is that the chemical reaction rate at any given moment is directly proportional to the rate of heat release:

$$d\alpha/dt = dH/dt \; 1/\Delta H_0,$$

where $d\alpha/dt$ is the reaction rate, dH/dt is the heat released per unit time or the heat flow, and ΔH_0 is the reaction heat determined from the peak area between the DSC curve and the baseline.

The degree of conversion (crosslinking) at the moment t is determined as a ratio between the heat released at this moment and the total heat of the reaction:

$$\alpha = \Delta H_t/\Delta H_0.$$

The aim of this work is to investigate the feasibility of using DSC to study the sulfur-accelerated vulcanization of rubbers using 1,4-*cis*-polyisoprene as an example.

MATERIALS AND METHODS

In the work, we used synthetic isoprene rubber (IR-3) (the content of 1,4-cis-links 92–99%, $M_n \approx 1 \times 10^6$). The vulcanizing group used per 100 weight units of rubber consisted of 2 weight units of sulfur, 1 weight unit of sulfonamide C, 5 weight units of zinc oxide, and 1 weight unit of stearic acid. The rubber was mixed with the vulcanizing group ingredients in a laboratory mill at room temperature. The vulcanization was studied with the use of a DSM-2m differential scanning microcalorimeter. The temperature and heat flow calibration was performed against standard samples of indium ($T_{\text{melt}} = 156.6°C$; $\Delta H_{\text{spec}} = 28.4419$ J/g). The mass of the sample under study was ∼ 25 mg. Under isothermal conditions, the sample was heated to the preset temperature at a heating rate of 64°/min. Then, isotherms were recorded. The time during which the thermal stability was attained was 90 s. The DSC isotherms were recorded at temperatures from 140 to 170°C. Under nonisothermal conditions, the samples were heated at a rate of 2, 4, 8, or 16°/min. The temperature
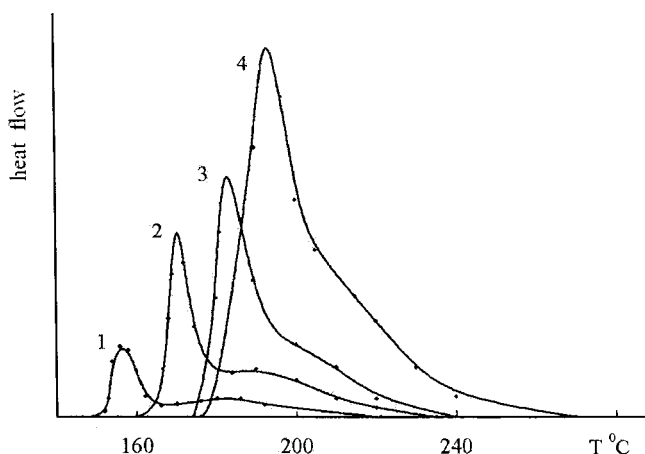
Figure 1 DSC thermograms of crosslinking IR for various scan rates: 2°/min (1), 4°/min (2), 8°/min (3), and 16°/min (4).

dependences were obtained at 40–250°C. The baseline was preset before each scanning experiment using two empty containers at a similar heating rate. The reaction was considered completed when the DSC curve reached the baseline. Weight losses of the samples after the experiments were insignificant—no more than 0.5% of the initial sample mass. The amount of heat released was determined from the peak area between the DSC curve and baseline. The accuracy of measurements was ±1°C for the temperature and ±5% for the heat of crosslinking.

The degree of crosslinking of samples heated in the calorimeter was determined from their equilibrium swelling in toluene.

RESULTS AND DISCUSSION

A preliminary study showed that heating of the mixture of IR and the vulcanizing group at a preset rate or constant temperature yields an exothermal peak of crosslinking; whereas heating of IR in a calorimeter in the absence of the vulcanizing group yields a monotonic curve. The thermograms of samples obtained at various heating rates are shown in Figure 1. The vulcanization stage is initiated at the temperature (T_{init}) of completion of the induction period; this is in agreement with the concept about the mechanism of vulcanization.[7] It is evident from Figure 1 that an increase in the scanning rate results in shifting the peak of crosslinking to the region of higher temperatures. From the thermograms obtained, the temperature of initiation (T_{init}) and the maximum rate (T_{max}) of crosslinking as well as the heat effect of the reaction at different scanning rates were determined. The total heat was calculated by the formula including the rate of heating of the sample.

TABLE I
Characteristics of IR Crosslinking
at Various Scanning Rates

| β (°/min)	T_{init} (°C)	T_{max} (°C)	ΔH_{spec} (J/g)
2	149	156	35
4	160	170	39
8	173	183	42
16	177	192	36

$$\Delta H_0 = 1/\beta \int_{T_1}^{T_2} dH/dt \, dT,$$

where β is the heating rate.

The temperature and specific heat of IR crosslinking at various scanning rates are listed in Table I. It is evident that the reaction heat increases slightly as the scanning rate is increased. At a high heating rate (16°/min), the specific heat of crosslinking decreases; the effect may be caused by the thermal decomposition of the bonds formed or by other secondary reactions that contribute to the total heat effect of the process.

The shift in the temperature of the peak crosslinking of rubber to the region of higher temperatures with increasing heating rate may be attributed to the influence of the molecular mobility in the chemical process. At a low heating rate, there is enough time for the chains to reach the states favorable for crosslinking. At a high heating rate, these states are attained later, at higher temperatures.

From the temperature dependences of IR crosslinking proceeding under isothermal conditions at various temperatures (Fig. 2), it is evident that the higher the temperature is, the sooner the crosslinking is initiated and the maximum rate is achieved.
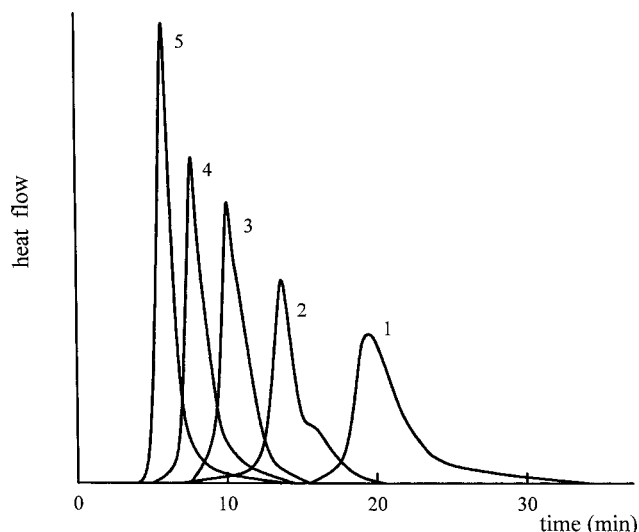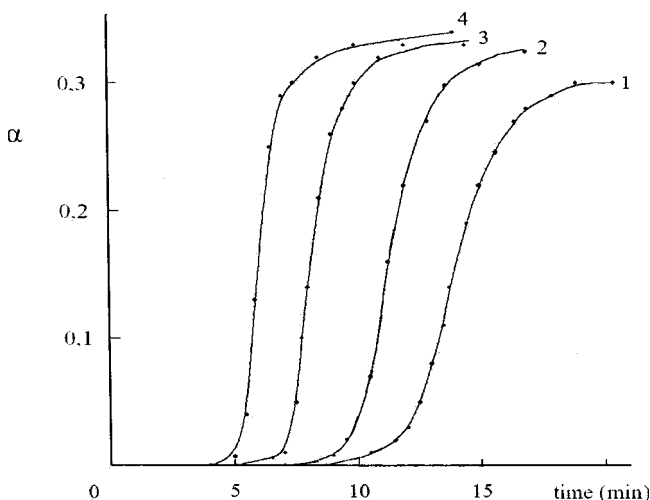

Figure 2 Isothermal DSC curves of crosslinking IR at 140°C (1), 145°C (2), 150°C (3), 155°C (4), and 160°C (5).

TABLE II
Characteristics of Isothermal IR Crosslinking

T (°C)	τ (min)	ΔH_{spec} (J/g)	V_{max} (10³) (s⁻¹)
140	15.5	14.0	1.0
145	7.5	12.0	1.0
150	7.0	13.0	2.0
155	5.0	13.0	3.0
160	4.0	13.0	3.5

From the peak areas of the isotherms, we determined the specific heats of crosslinking; their values are listed in Table II. According to data shown in Table II, the heat of crosslinking proceeding under isothermal conditions varies slightly with increasing the temperature; however, it remains lower than the maximum heat of nonisothermal crosslinking. This is evident for an incomplete crosslinking of rubber under isothermal conditions.

The degree of crosslinking achieved by the time t was determined as $\alpha = \Delta H_t / \Delta H_0$, where ΔH_0 is the heat of crosslinking of rubber under nonisothermal conditions at a heating rate of 4°/min. Figure 3 shows the kinetic curves of the IR vulcanization proceeding under isothermal conditions at various temperatures. In all the cases, we observe a drastic increase in the crosslinking rate after the end of the induction period (τ). The induction period (the absence of a recordable heat effect) involves melting and interactions of the vulcanizing group components; these processes are associated with an insignificant total heat effect. The quasi-stationary segment of the kinetic curve corresponds to the period of formation of crosslinks between macromolecules. From the kinetic curves, we determined the maximum rate and the effective energy of activation of IR crosslinking with the vulcanizing group chosen. The values of the reaction rates (V_{max}) are listed in Table II.

On the basis of the literature data[2] and measurement results on the heat release, the kinetic model of crosslinking of rubber was constructed. The period of crosslinking may be described by the first-order equation:

$$d\alpha/dt = k(1 - \alpha),$$

where k is the reaction rate constant. With regard to the temperature dependence of k, we get the equation for the rate of the reaction proceeding under isothermal conditions

$$d\alpha/dt = A \exp[-E_a/RT](1 - \alpha),$$

where A and E_a are the pre-exponential multiplier and energy of vulcanization, respectively; R is the gas constant equal to 8.314 J/mol K; and T is the temperature (in Kelvin).

The effective energy of activation of crosslinking was calculated in different ways: by the Arrhenius equation,

$$\ln(d\alpha/dt) = \ln(dH/dt \; 1/\Delta H_0)$$
$$= \ln A - E_a/RT + \ln(1 - \alpha)$$

and from the shift in the temperature of the crosslinking exotherm peak depending on the heating rate β; it is calculated by the Ozawa equation[8]

$$\ln \beta = \text{constant} - 1.052 E_a/RT_{max}$$

The value of E_{aeff} determined from the maximum rates of IR crosslinking at various temperatures under isothermal conditions (91 kJ/mol) is similar to that calculated from the shift in the temperature of

Figure 3 Kinetic curves of crosslinking IR at 145°C (1), 150°C (2), 155°C (3), and 160°C (4).
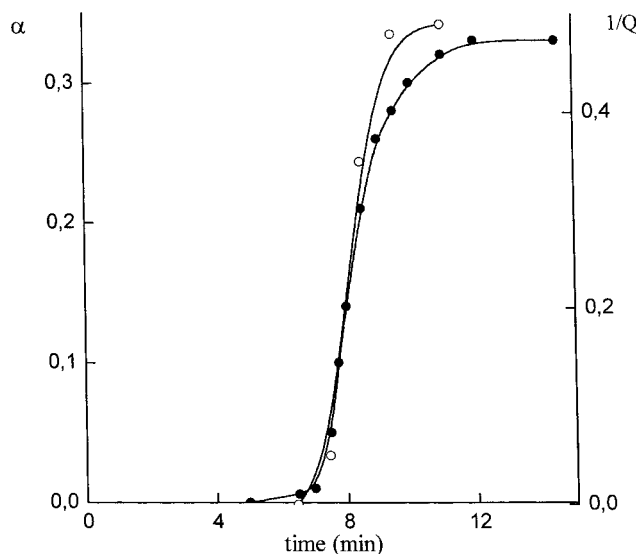
Figure 4 Dependence of IR crosslinking degree on time, determined by the methods of DSC (●) and equilibrium swelling (○) at 155°C.

the crosslinking peak at various heating rates under nonisothermal conditions (88 kJ/mol). Note that the calculated energy of activation and the temperature coefficient of the reaction, which is equal to 2, are consistent with the literature data on the sulfur-accelerated vulcanization.[7]

The fact that heat released during heating the samples is determined by crosslinking is verified by the data on equilibrium swelling of samples heated in the calorimetric cup during different times at the same temperature.

Figure 4 shows the dependences of the IR crosslinking degree (kinetic curves) (155°C) determined by the methods of DSC and equilibrium swelling (in the latter case, the value $1/Q$, which is proportional to the crosslinking degree, is determined). As is seen from Figure 4, the shapes of the crosslinking curves are similar.

Thus, differential scanning calorimetry is a rapid and convenient method of studying the whole process of sulfur-accelerated vulcanization including the induction period. The kinetic parameters determined in this work (duration of the induction period, rate of vulcanization, and effective energy of activation) are consistent with the literature data.

References

1. Ishida, H.; Rodriguez, Y. Polymer 1995, 36, 3151.
2. Boey, F. Y. C.; Qiang, W. Polymer 2000, 41, 2081.
3. Starink, M. J. Thermochim Acta 2003, 404, 163.
4. Chough, S.-H.; Chang, D.-H. J Appl Polym Sci 1996, 61, 449.
5. Simon, P.; Kusma, A. J Therm Anal Calorimet 1999, 56, 1107.
6. Bershteyn, V.A.; Egorov, V. M. Differential Scanning Calorimetry for Physicochemistry of Polymers; Chimiya: Leningrad, 1990; p 221.
7. Dogadkin, B. A.; Donczov, A. A.; Shershnev, V. A. Chemistry of Elastomers; Chimiya: Moskva, 1981; 373 pp.
8. Ozawa, T. J Therm Anal 1976, 9, 369.