Fig. 2. Appearance of vulcanizates after 8 weeks in sunlight. (*a*) Dicumyl peroxide vulcanizate with 2246 only. (*b*) Dicumyl peroxide vulcanizate with 2246 and Tinuvin P. (*c*) Sulfur accelerator vulcanizate with 2246 only. (*d*) Sulfur accelerator vulcanizate with 2246 and Tinuvin P.

sulfur stock occurred in presence of Antioxidant 2246 and Tinuvin P, while in absence of the absorber very pronounced crazing had occurred.

It is suggested that a combination of uv absorber and nonstaining antioxidant effectively protects transparent vulcanizates against sunlight ageing. In filled stocks the absorber is not so useful since the filler itself acts as a light screen.

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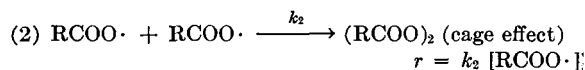Welwyn Garden City, Herts
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Control of Temperature Rise in Crosslinking of Unsaturated Polyesters by the Use of Gamma Radiation Initiation
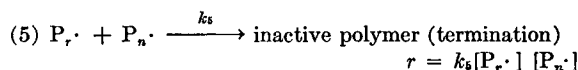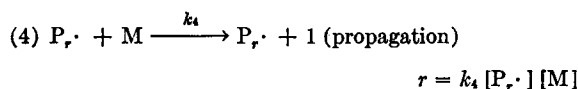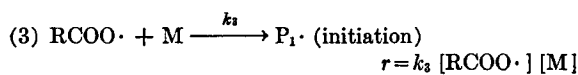
Introduction

Schulz[1] and others have shown that the kinetics of free-radical initiated vinyl polymerization follow the kinetic equation

$$dM/dt = K_1[C]^{1/2} [M] [K_2M/(1 + K_2M)]^{1/2}$$

Matheson[2] in a subsequent paper gave theoretical justification for this behavior on the basis of a "cage effect." The following reactions were assumed to take place

(1) $(RCOO)_2 \xrightarrow{k_2} 2RCOO\cdot$ $r = k_1 ([RCOO])_2$

(2) $RCOO\cdot + RCOO\cdot \xrightarrow{k_2} (RCOO)_2$ (cage effect)
$$r = k_2 [RCOO\cdot]$$

(3) $RCOO\cdot + M \xrightarrow{k_3} P_1\cdot$ (initiation)

$$r = k_3 \, [RCOO\cdot] \, [M]$$

(4) $P_r\cdot + M \xrightarrow{k_4} P_r\cdot + 1$ (propagation)

$$r = k_4 \, [P_r\cdot] \, [M]$$

(5) $P_r\cdot + P_n\cdot \xrightarrow{k_5}$ inactive polymer (termination)

$$r = k_5[P_r\cdot] \, [P_n\cdot]$$

On the basis of this scheme in which step (2) is assumed to be first order, K_1 is shown to be $k_4/k_5^{1/2}$ and K_2 is shown to be k_3/k_2. The kinetic equation of Matheson is

$$\frac{d[M]}{dt} = \frac{k_4}{k_5^{1/2}} \, [C^{1/2}] \, [M] \left[\frac{k_1 k_3/k_2 \, [M]}{1 + (k_3/k_2)[M]} \right]^{1/2}$$

In a subsequent paper[3] Schulz and Blaschke noted sharp temperature rises during the polymerization of methyl methacrylate using benzoyl peroxide as the initiating catalyst. This is a general property of bulk polymerizations of vinyl-type monomers. This can be predicted on the basis of the exothermicity of the polymerization reaction. Since the rate constants will increase with increasing temperature in accordance with the Arrhenius Law

$$K = Ae^{-E/RT}$$

it follows that the exotherm of the polymerization will tend to increase the rate of polymerization, as well as the rate of production of initiating free radicals.

The limit to this is provided by (a) the disappearance of monomers as the polymerization proceeds, (b) the increase in the rate of the termination reaction, and (c) the loss of heat from the polymerizing mass by conduction.

Of these three effects, the first is most important since, in Matheson's equation,[2] the termination reaction constant appears as a reciprocal square root, and the loss of heat by conduction is a slower process than the generation by propagation, until the overall reaction rate falls off to a considerable extent. Furthermore, the loss of heat by conduction is obviously dependent on the geometry; i.e., size and shape of the specimen.

The crosslinking of unsaturated polymers is essentially a vinyl copolymerization. The chemistry of this class of resinous materials is described in several places.[4] The three-dimensional network required for gelation[5] is attained by the copolymerization of vinyl monomers (styrene, diallyl phthalate) with points of unsaturation on polyester chains. The temperature rises generated by the crosslinking of these resins are discussed by Nichols and Bliss,[7] and others.[8]

If the kinetics of Schulz and Matheson are applicable to unsaturated polyesters, even in a general way only, then removal of the catalyst should stop the propagation reaction and only the termination reaction should proceed. The use of radiation initiation instead of chemical catalysts (e.g., organic peroxides) would permit this, if the kinetics of radiation-induced crosslinking were similar to those of the chemically initiated reaction.

Burlant and Adicoff[9] showed that polymerization induced by electron radiation occurs in separate volume elements and that the degree of polymerization is a function of total dose rather than dose rate. Collinson, Dainton, and McNaughton[10] used γ-radiation and showed that the rate of polymerization was linear with dose rate and dependent

on the concentration of monomers. This would indicate that, except for the complications brought on by the dissociation of the catalyst and the concomitant cage effect, the kinetics of radiation-induced polymerization are, indeed, similar to the kinetics of the chemically initiated reaction.

EXPERIMENTAL

Various quantities of Hetron 92 (Hooker Electrochemical Corp.) polyester were crosslinked in bulk by chemical catalysis and by γ-radiation from a cobalt-60 source. The chemically catalyzed samples contained 1% methyl ethyl ketone peroxide (Lupersol DDM, Lucidol Division, Wallace & Tiernan, Inc.) and 0.05% cobalt naphthenate. The materials were hand-mixed and poured into vials. A thermocouple was inserted at approximately the geometric center
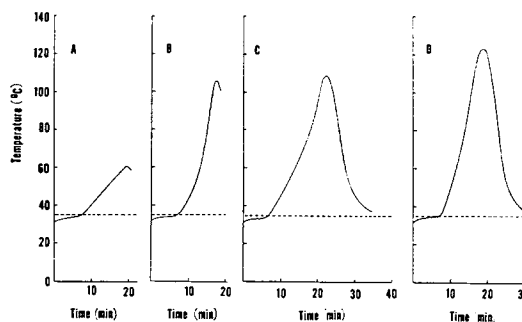

Fig. 1. Polymerization of Hetron by a catalyst. Sample diameter (in.): $^{11}/_{16}$. Sample length (in.): A, 0.719; B, 1.125; C, 1.563; D, 1.531.
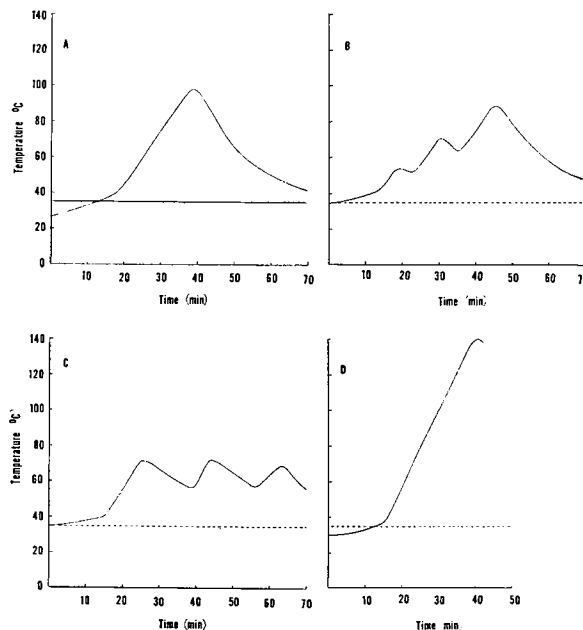

Fig. 2. Polymerization of Hetron by radiation. Sample diameter (in.): A–C, $^{11}/_{16}$; D, ca. 1.5. Sample length (in.): A and B, 1.719; C, 2.031; D, ca. 12. Radiation: A and D uninterrupted; B and C interrupted.

of the sample and the vials were placed in a 35°C. water bath.

The radiation-initiated samples merely had thermocouple inserted and were placed inside a cobalt-60 source of 487,000 r/hr. strength having the shape of a hollow cylinder with an inside diameter of 1.8 inches and a length of 13.5 inches. Temperature was continuously recorded for each sample.

RESULTS

The temperature vs. time curves for those samples crosslinked catalytically are given in Figure 1. The curves for those samples crosslinked by radiation are given in Figure 2. Interruptions in dosage are indicated in the figures.

DISCUSSION

The effect of sample size and shape can be seen by comparing A–D of Figure 1. The temperature attainable with a large sample, using uninterrupted radiation, is shown in D of Figure 2. As is pointed out by the monograph of the Bjorksten Laboratories,[8] the rate of heat generation and therefore the maximum temperature attainable can be controlled to some extent by controlling such things as catalyst concentration, accelerator concentration, and initial temperature as well as the chemistry of the resin itself.

However, as is shown in C of Figure 2, any desired maximum temperature can be held as a limit using γ-radiation catalysis. Furthermore, this limit is completely arbitrary and independent of the particular resin involved.

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