

Thermoplastic Elastomers Via Radical Polymerization. I.

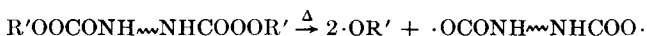
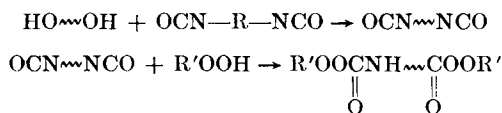
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Synopsis

Thermoplastic elastomers were synthesized using a method for preparation of block copolymers introduced by Tobolsky and Rembaum. A hydroxy-terminated polyester or polyether was chain extended with tolylene diisocyanate and capped with cumene hydroperoxide. The high molecular weight peroxy-carbamate was used as initiator for polymerization of styrene, methyl methacrylate, or acrylonitrile monomer. Their physical properties were investigated by modulus-temperature curves. The effect of composition on modulus was also examined.

INTRODUCTION

Some time ago, Tobolsky and Rembaum¹ proposed a new method of synthesizing block copolymers. The reaction scheme was the following:



The free radicals initiate further polymerization of a vinyl monomer. A modification of this method² uses a bishydroxyperoxide instead of a hydroperoxide to eliminate the vinyl homopolymer always produced from the alkoxy radicals.

In view of the attractive properties that thermoplastic elastomers have,³ we have attempted to employ this method to synthesize this type of material. Thermoplastic elastomers are block copolymers of ABA type, where A is a glassy thermoplastic and B is an elastomer. Thus, a hydroxy-terminated polyester or polyether was chain extended first with a diisocyanate and then capped with a hydroperoxide to form a polymeric peroxy-carbamate, which then was used as initiator for vinyl polymerization.

Experimental evidence, however, as well as theoretical predictions suggest two critical factors that limit the use of this method. These are the efficiency of the peroxy-carbamate as initiator for vinyl polymerization and the

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extent of the condensation reaction. Because of these two factors, the product will always contain high portions of B- and AB-type molecules, especially when high molecular weight peroxyurethane is desired. For that reason we approached the problem in two ways. One was to use a branched middle-block segment, so that even if the extent of the condensation step or the efficiency of the peroxyurethane were not 100%, the fraction of ABA-type block molecules would remain high.^{4,5} The other was to use aromatic diisocyanates so that the aromatic groups would form blocks within the middle-block segment, and therefore capping both ends with vinyl polymer would not be quite so critical. In this way one modifies the properties of the pure polyurethane by incorporating an additional phase in the blocks, e.g., different solubility properties, different modulus, one more T_g , etc.

In this work, we made some block copolymers by chain extending polyester glycol of M_n of about 3000 with tolylene diisocyanate (TDI) and capping with cumene hydroperoxide (CHP). In a second stage, this was used to initiate vinyl polymerization. The properties of the product were studied by modulus-versus-temperature curves.

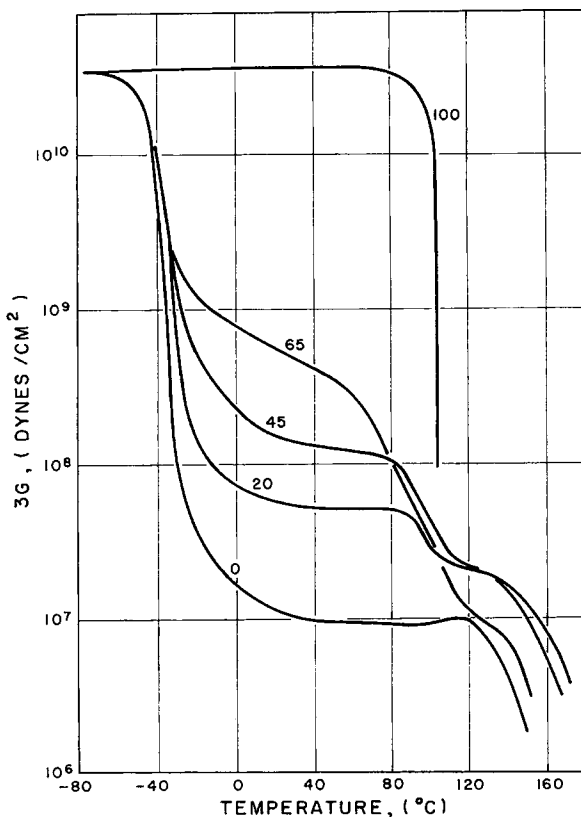


Fig. 1. Polyester-polystyrene block copolymers. Numbers indicate per cent polystyrene.

EXPERIMENTAL

Styrene was washed with a 10% NaOH solution and dried over calcium hydride. Methyl methacrylate (MMA) was washed with 10% NaOH and dried over Linde-type 5A molecular sieves. Toluene diisocyanate (TDI) was used as commercially available. Cumene hydroperoxide (CHP) was dried over MgSO_4 . Polyester glycol (PE) was vacuum dried for several days.

The reaction was carried out in a one-shot two-step method. All the reactants were mixed together and allowed to react at room temperature in the presence of MgO as catalyst. Then the temperature was raised to initiate vinyl polymerization. The following is a specific example.

Example. 5.231 g PE (1360) (7.7×10^{-3} equiv.), 0.0735 g CHP 80% pure (3.86×10^{-4} equiv.), 0.7019 g TDI (7.76×10^{-3} equiv.), 1.224 g styrene monomer, 5 ml toluene, and 0.3 g MgO were mixed under stirring at room temperature in a glass, screw-capped bottle. After 48 hr at room temperature, the bottle was placed in a high-temperature bath at 90°C for

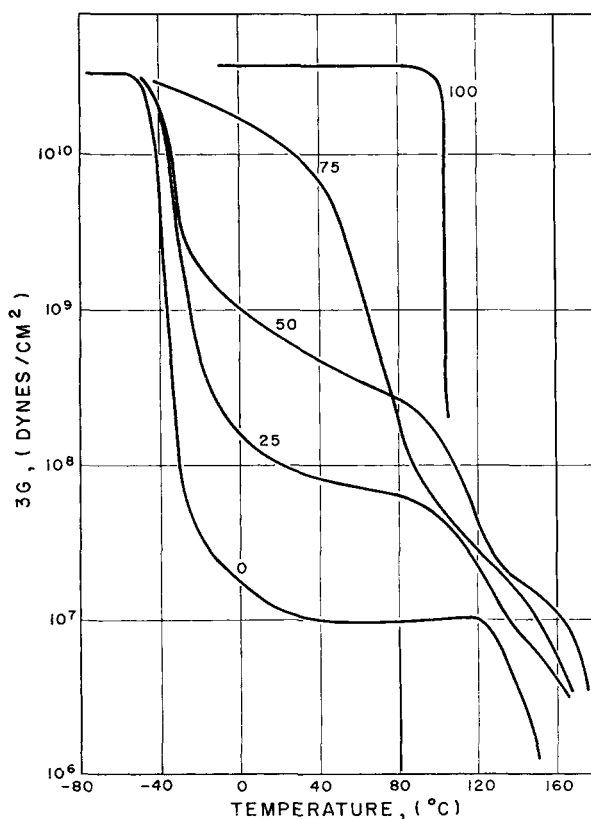


Fig. 2. Polyester-poly(methyl methacrylate) block copolymers. Numbers indicate per cent PMMA.

another 24 hr. The product was vacuum dried and press molded at 40,000 psi at 280°F for 10 min. It was soluble in hot DMSO (60°C).

RESULTS

In order to avoid crosslinking via allophanate or biuret formation, the reactants were mixed so that NCO and OH + OOH groups were close to equivalent amounts. MgO was reported⁸ to catalyze the extension reaction more than the side reactions, and for that reason it was used as a catalyst.

Figures 1, 2, and 3 show the modulus-temperature curves of a series of block copolymers. The -50°C and +140°C transitions are attributed to the polyurethane segments, specifically to polyester and aromatic diisocyanate blocks, respectively. The vinyl polymer phase shows one addi-

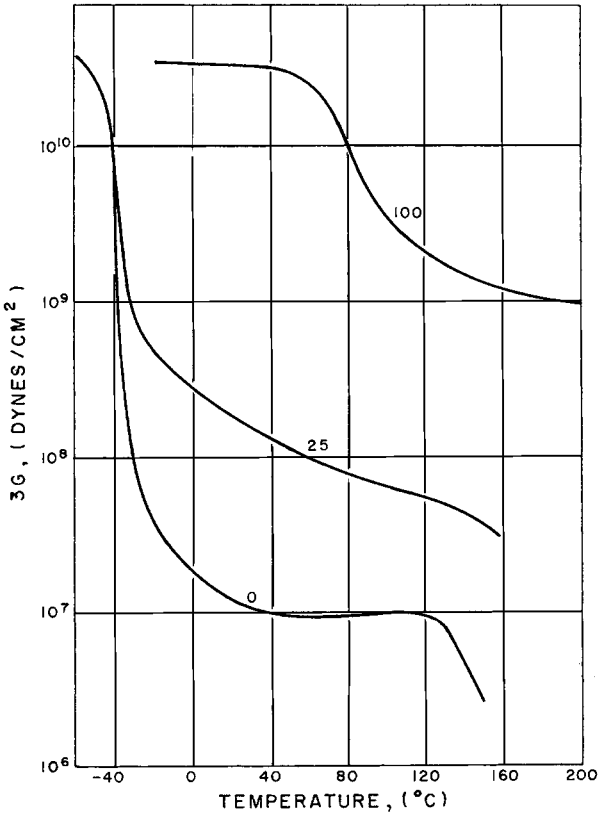


Fig. 3. Polyester-polyacrylonitrile block copolymers. Numbers indicate per cent PAN.

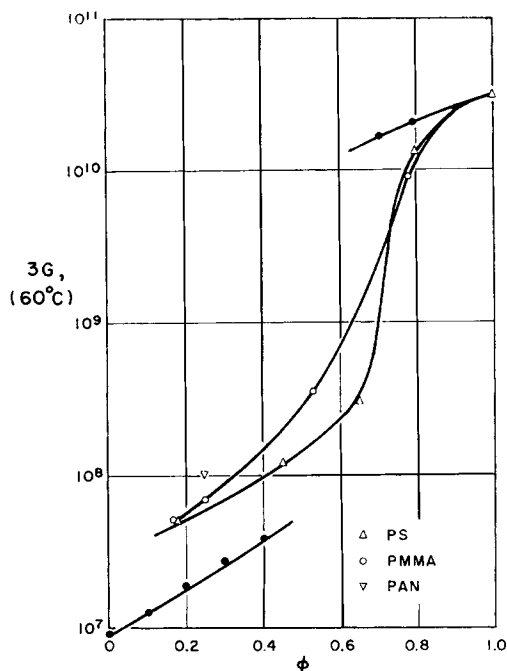


Fig. 4. Modulus at 60°C versus copolymer composition: (Δ) PS; (○) PMMA; (▽) PAN; (●) calculated values.

tional transition at the T_g of the polymer, e.g., 100–105°C for polystyrene and PMMA. Polyacrylonitrile block copolymers maintain their high modulus above 140°C because of the crystallinity of the PAN phase.

Figure 4 represents a plot of $3G$ versus Φ , where Φ is the volume fraction of the vinyl polymer. In the same figure there are the theoretically predicted curves from the Guth-Smallwood^{7,8} and Mackenzie⁹ equations (or from Kerner's¹⁰ equation) for filled rubber. The moduli of the rubbery and the glassy materials were taken as those of pure polyurethane and pure PMMA or PS. A reference temperature of 60°C was used. The predicted curves for the Guth equation,⁸ at low Φ and the Mackenzie equation⁹ at high Φ are shown as filled circles.

The difference in the slope of the modulus-temperature curves in the plateau region between samples of the same composition but different vinyl polymer is attributed to a certain degree of compatibility between PE and PAN or PMMA phases. Because of this, PE-PMMA samples showed leather-like behavior while PE-PS samples were more rubbery.

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