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A New Class of Block Polymers

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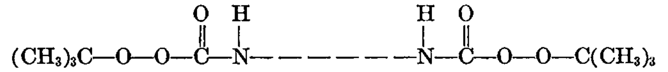
Synopsis

The reaction of industrially available "prepolymers," containing one or several isocyanate groups per chain, with *tert*-butyl hydroperoxide yielded long-chain peroxycarbamates. These were found able to initiate the polymerization of a wide variety of vinyl monomers as well as dienes leading to a new class of block polymers of very interesting physical properties. Polyether and polyester "prepolymers" with one, two, or three isocyanate functionalities were linked chemically to polystyrene, polymethyl methacrylate, poly-*n*-butyl acrylate, polyarylonitrile, and polyisoprene. The formation of block polymers was proved by both physical and chemical methods. Their mechanical properties were illustrated by means of torsional modulus-temperature curves. The effect of varying composition and of a crosslinking agent on the elastic modulus was examined. Tentative reaction mechanisms were also presented.

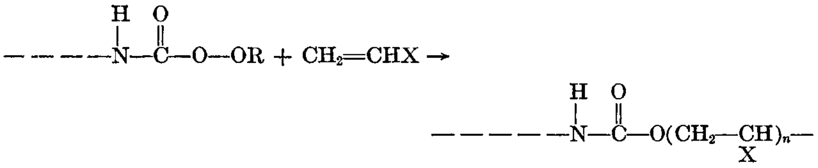
The purpose of this work was to synthesize a new type of block polymers by the chemical combination of low molecular weight polymers of inherently rubbery properties, such as polypropylene oxide, with polymers of basically glassy properties, such as polystyrene or polymethyl methacrylate. The final product would have the desirable characteristics of both: a rubbery component capable of imparting impact resistance and a glassy component capable of imparting a high modulus of elasticity over a wide temperature range. In order to accomplish this we proposed to react polypropylene oxide diisocyanate with *tert*-butyl hydroperoxide to form a diperoxycarbamate represented by the following formula:



$$(CH_3)_3C{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}-\,-\,-\,-\,-\,-\,-{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}C(CH_3)_3 \qquad (1)$$

where the dashed line represents a polypropylene oxide chain.

The peroxycarbamate groups were expected to react similarly to the peroxides commonly employed, i.e., to initiate growing radical chains of vinyl monomers by the reaction:



$$-\,-\,-\,-\,-{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}OR + CH_2{=}CHX \rightarrow -\,-\,-\,-\,-\,-{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O(CH_2{-}\underset{X}{CH})_n{-} \qquad (2)$$

where R represents a tertiary butyl group, n an integer, and X a halogen, CN, phenyl, etc.

The application of the ideas outlined above and the characterization of the products obtained constitute the subject of this paper.

EXPERIMENTAL

Materials

Styrene and isoprene were thoroughly dried with calcium hydride and fractionally distilled. Methyl methacrylate and *n*-butyl acrylate were washed with a 3% NaOH solution, dried with calcium chloride, and fractionally distilled. Acrylonitrile and tetraethyleneglycol dimethacrylate were passed through a column of silica gel immediately before use. Benzene and *n*-heptane were distilled from sodium and kept over calcium hydride. Commercial *tert*-butyl hydroperoxide of 90% purity was steam distilled and the first fraction rejected. The main distillate, after separation from water, was repeatedly dried over magnesium sulfate. The formation of block polymers, however, proceeded equally well when commercial *tert*-butyl hydroperoxide dried with magnesium sulfate was used. 2,4-Tolylene diisocyanate was fractionally distilled before use.

Formation of Block Polymers

Block polymers were formed from the reaction of low molecular weight polymers, terminated with one or several isocyanate groups (industrially known as prepolymers), with TBH and with vinyl monomers.

A polyether prepolymer diisocyanate was prepared from the reaction of a hydroxy-terminated polypropylene oxide (two hydroxyl groups per polymeric chain, molecular weight about 1800) with 2,4-tolylene diisocyanate. A polyester prepolymer diisocyanate was prepared from the reaction of a hydroxy-terminated polyester of adipic acid, ethylene glycol, and propylene glycol (two hydroxyl groups per polymeric chain, molecular weight about 2000), with 2,4-tolylene diisocyanate. The trifunctional prepolymer consisted of castor oil (mixed glycerides of ricinoleic and oleic acid, the main fraction of which has three hydroxyl groups per chain) that had reacted with 2,4-tolylene diisocyanate. Finally, a polyether prepolymer monoisocyanate resulted from the reaction of polypropylene oxide with one hydroxyl group per chain (molecular weight about 900) and 2,4-tolylene diisocyanate. The amounts of free isocyanate groups could be determined by chemical or infrared (IR) analysis.

The block polymers were prepared in evacuated and sealed Pyrex flasks or in glass containers in the presence of oxygen (with equal success) by a two-step or one-step procedure, as illustrated by the following examples.

Example 1. 4.2 g. of polyester prepolymer diisocyanate was dissolved in benzene in a 100 cc. pyrex flask provided with a S/T joint. A 1 g. amount of *tert*-butyl hydroperoxide was added. The mixture was left at room temperature for 60 min. and the prepolymer diperoxycarbamate precipitated with *n*-heptane. The liquid phase was decanted with the process of dissolution and precipitation repeated twice. The remaining traces of solvent and hydroperoxide were then removed by pumping for 6 hrs. under high vacuum at 30°C. Styrene (5.8 g.) was next added to the flask contents and the mixture degassed by freezing and thawing three times in the high vacuum system. The flask was then sealed off at a pressure of 10^{-6} mm. Hg and heated in an oven at 73 ± 2°C. The originally liquid mixture solidified within 4 hrs. After a total heating of 24 hrs. the polymer obtained was extracted with benzene in a Soxhlet apparatus and dried in a vacuum at 60°C. for 24 hrs. The loss of weight after extraction amounted to 20% of the solid polymer. The dry extracted polymer was molded between plates of a hydraulic press at 250°F. and 30,000 psi. for 10 min.

The torsional modulus of the film obtained was determined by means of a Gehman tester and is shown in Fig. 2. Methanol was added to the benzene extract and the precipitate obtained, after filtering and drying, amounted to 3% of the total polymer. The IR analysis of this precipitated material showed the presence of polystyrene homopolymer contaminated with impurities which were not identified.

Example 2. Polyether prepolymer diisocyanate, 6.6 g., was dissolved in 23.9 g. of acrylonitrile in a glass container provided with a tight glass lid. A 0.6 g. amount of *tert*-butyl hydroperoxide was added to the mixture and the whole kept for 1 hr. at room temperature in the closed glass container. At the end of this time it was placed in an oven maintained at 73 ± 2°C. After being heated for 24 hrs. the polymer was removed and molded at 250°F. for 10 min. at a pressure of 30,000 psi. The elastic modulus temperature curve of the clear and tough film obtained is shown in Fig. 4.

Example 3. The following components, given as gram amounts, were mixed in dry screw-cap bottles for three experiments.

	1	2	3
Polyether prepolymer diisocyanate	10.58	11.46	22.7
Isoprene	28.23	11.40	7.2
tert-Butyl hydroperoxide	1.0	1.0	2.0
Pyridine (dried with KOH)	0.05	0.05	0.05

The three mixtures solidified after being kept at 60°C. for 12 hrs. Heating was continued for an additional period of 12 hrs. at 100°C. Three rubbery solids were obtained which showed no loss of weight after extraction with methanol. The torsional moduli of rubbers prepared in experiments 1 and 3 were determined and is shown in Fig. 7.

Example 4. Monohydroxy polypropylene oxide (molecular weight 886 calculated from hydroxyl number data), 164.2 g., was mixed with 33.6 g. of freshly distilled 2,4-tolylene diisocyanate and left to react for 36 hrs. at room temperature. The homogeneous yellow viscous liquid was heated, at the end of this time, in a nitrogen atmosphere for 2 hrs. at 100°C. IR analysis and hydroxyl number determination proved that the reaction went to completion. The polyether monoisocyanate thus prepared was mixed in a 6.55 g. amount with 19.31 g. of styrene, 0.3 g. of *tert*-butyl hydroperoxide, and 0.025 g. of pyridine. The homogeneous mixture was heated at 60 ± 2°C. for 12 hrs. and at 100 ± 2°C. for 24 hrs. The solid formed was dissolved in 100 cc. of tetrahydrofuran, precipitated with 1 l. of methanol, filtered, washed with methanol, and dried at 60°C. under vacuum for 24 hrs. The dry polymer was molded at 250°F. and 30,000 psi for $^1/_2$ hour. A clear transparent film was obtained. The same amount of polyether monoisocyanate (6.55 g.) treated, under the same conditions, with 0.3 g. of *tert*-butyl hydroperoxide yielded a product which was completely soluble in methanol.

Series. Under similar experimental conditions a series of block polymers was prepared with varying proportions of *n*-butyl acrylate methyl methacrylate, styrene, and isoprene, etc. The yields of polymers obtained by the above-described procedures, after methanol extraction, ranged between 75 and 98%.

Evolution of a small amount of gas was observed only in a very few experiments; in the majority of about 100 runs there was no apparent formation of carbon dioxide.

Reaction of 2,4-Tolylene Diisocyanate

Reaction of 2,4-tolylene diisocyanate with *tert*-butyl hydroperoxide in the presence of styrene.

tert-Butyl hydroperoxide (1.1 g.), styrene (9 g.), 2,4-tolylene diisocyanate (1.1 g) and pyridine (0.025 g) were mixed at −30°C. and kept at 0°C. for 12 hours. The dark-colored solidified mixture, stirred with methanol, filtered and dried in vacuum at 60°C. for 12 hrs., yielded 5 g. of material, 10% of which was insoluble in benzene. The IR spectrum of the material soluble in CS_2 showed all the characteristic absorption peaks of polystyrene, in addition to a band at 3.02 μ which may be attributed to an NH group.

Preparation of Hydroxy-Terminated Polystyrene

Styrene (22 g.) was polymerized by means of *tert*-butyl hydroperoxide (2 g.) in similar conditions to those used in the preparation of block polymers, i.e., in presence of 0.05 g. of pyridine and being heated in a closed glass container at 73°C. for 12 hrs. and at 100°C. for an additional 12 hrs. The polystyrene (18 g.) was isolated in the usual way. The IR spectrum (0.8 g./100 cc. of CS_2, 1 mm. cell) showed an absorption peak at 2.76 μ. A more detailed IR analysis (with lithium fluoride optics) confirmed this finding. The molecular weight of the polystyrene determined by the Rast camphor method was found to be equal to 1080. A total of 99.9% for the CH content was found by elementary analysis.

Analytical Methods

IR spectra were obtained by means of a Perkin-Elmer Model 21 spectrophotometer with a NaCl prism for the wavelength range of 2 to 15 μ. A similar instrument fitted with a lithium fluoride prism was used for the 2.74 to 3.14 μ range. (Solvent: CCl_4, 1 cm. quartz cell.)

The estimation of NCO groups in prepolymers was achieved either spectrophotometrically, the extinction coefficient at 4.4 μ, or by the determination of the amine equivalent as described by Dombrow.[1] The hydroxyl content was determined according to the method of Ogg et al.[2] The hydroperoxide content was estimated iodometrically by the method of Price and Morita.[3] The determination of the torsional modulus over various temperature ranges was carried out by means of a Gehman tester. X-ray diffraction patterns were obtained through the courtesy of Dr. V. D. Gupta of the Textile Research Institute in Princeton, New Jersey.

RESULTS AND DISCUSSION

Mechanical Properties of Block Polymers

Figures 1–7 represent the elastic modulus–temperature spectra of a wide variety of block polymers, the preparation of which is described under Experimental. A brief review of the practical and theoretical significance of elastic modulus temperature curves with reference to random copolymers, homopolymers, blends, graft and block polymers, has been recently published.[5] The shapes of the curves in Figures 1–5 constitute strong evidence of the formation of block polymers with unusual properties. Random copolymers have sharp glass transition temperatures while grafts and blocks exhibit a gradual change of the elastic modulus[6,7] over a wide temperature range, as found in Figures 1–5. A comparison of the curves also shows the gradual shift of the elastic moduli with the variation in the relative proportion of the reactants. Figures 3, 5, and 6 show the effect of a crosslinking agent on the mechanical properties of blocks. Where the rubbery plateau is absent, crosslinking does not occur to any significant extent. This is confirmed by the fact that polyether and polyester–styrene, as well as acrylonitrile and methyl methacrylate blocks, could be molded at relatively low temperatures and short times of contact in spite of their limited solubility in common organic solvents.

The effect of crosslinking is apparent in Figures 3, 5, and 6. The upward shift of the elastic modulus with increasing amounts of crosslinking agent (tetraethylene glycol dimethacrylate) is considerable. It is also not surprising to find a rubbery plateau in the curves representing blocks which were prepared with trifunctional reactants (castor oil triisocyanate, Fig. 7); the shapes of curves 1 and 2 of Figure 7 indicate, however, that considerable adventitious crosslinking had taken place during the formation of isoprene blocks.

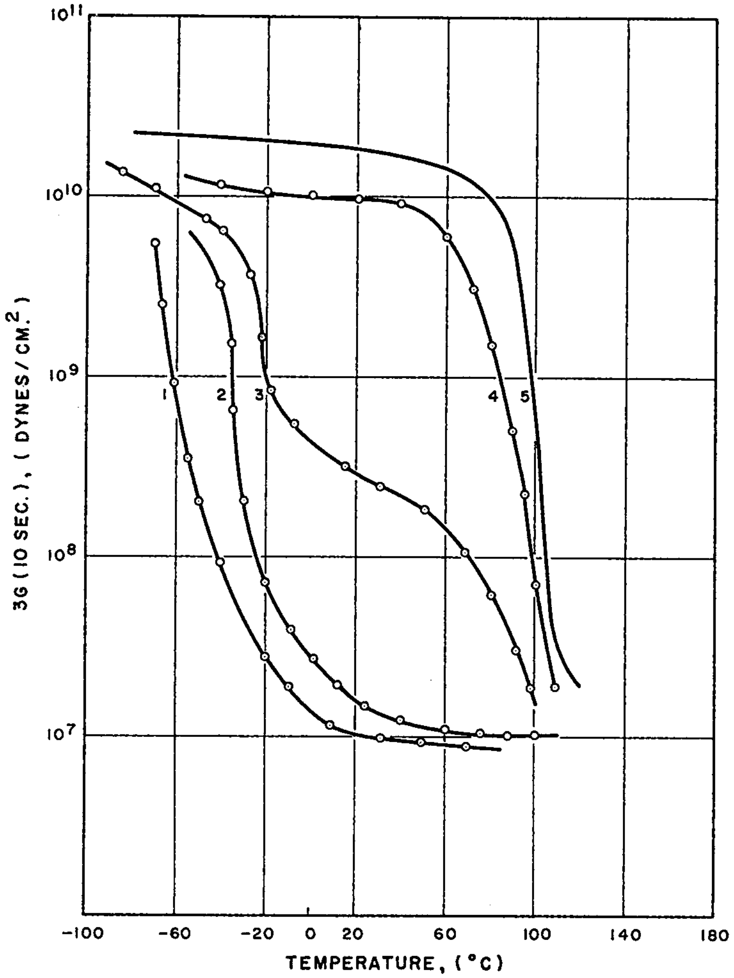
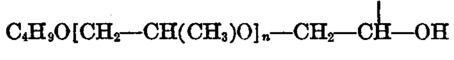


Fig. 1. Propylene oxide–styrene block polymers. Percentage polyether prepolymer: (*1*) reacted with ethylenediamine; (*2*) 75%, styrene 25%; (*3*) 50%, styrene 50%; (*4*) 24.1%, styrene 75.9%; (*5*) pure polystyrene.

Additional Proof of Block Polymers

Polypropylene oxide of the structure:



$$C_4H_9O[CH_2{-}CH(CH_3)O]_n{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}OH \qquad (3)$$

with the hydroxyl number of 63.4 mg. KOH/g., reacted with a slight excess of 2,4-tolylene diisocyanate as described under Experimental. The course of this reaction could be followed by means of IR in the 3 μ region. In Figure 8 are shown the spectra of the propylene oxide before reaction, 5 hrs. after mixing, and 24 hrs. after mixing.

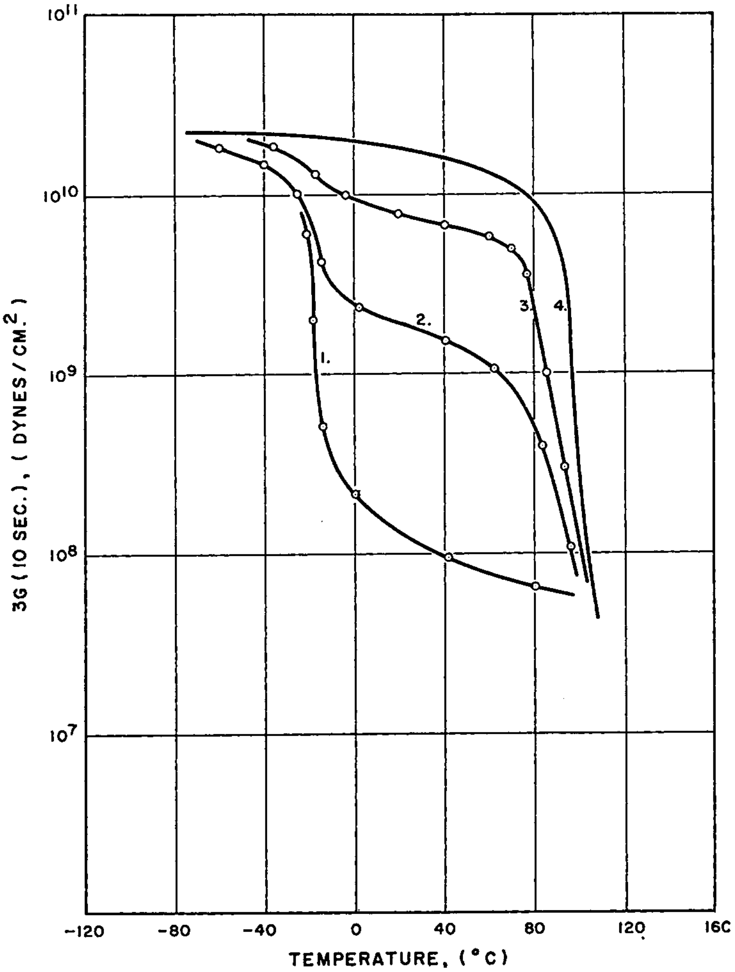
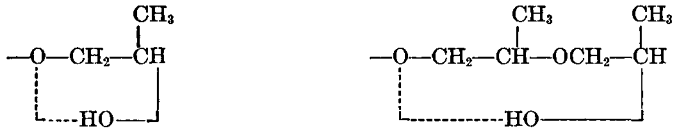


Fig. 2. Polyester–styrene block polymers. Percentage polyester prepolymer: (*1*) reacted with ethylenediamine; (*2*) 42%, styrene 58%; (*3*) 25%, styrene 75%; (*4*) pure polystyrene.

The 2.76 and 2.87 μ peaks (Fig. 8, *A*) are due[8] to H-bonded OH groups of the type:



$$-O-CH_2-\overset{CH_3}{\underset{HO}{CH}} \qquad -O-CH_2-\overset{CH_3}{CH}-OCH_2-\overset{CH_3}{\underset{HO}{CH}} \qquad (4)$$

After a standing of 5 hrs. at room temperature the intensity of the OH absorption peaks decreased and NH peaks at 2.9, 2.98, and 3.02 μ appeared (Fig. 8, *B*).

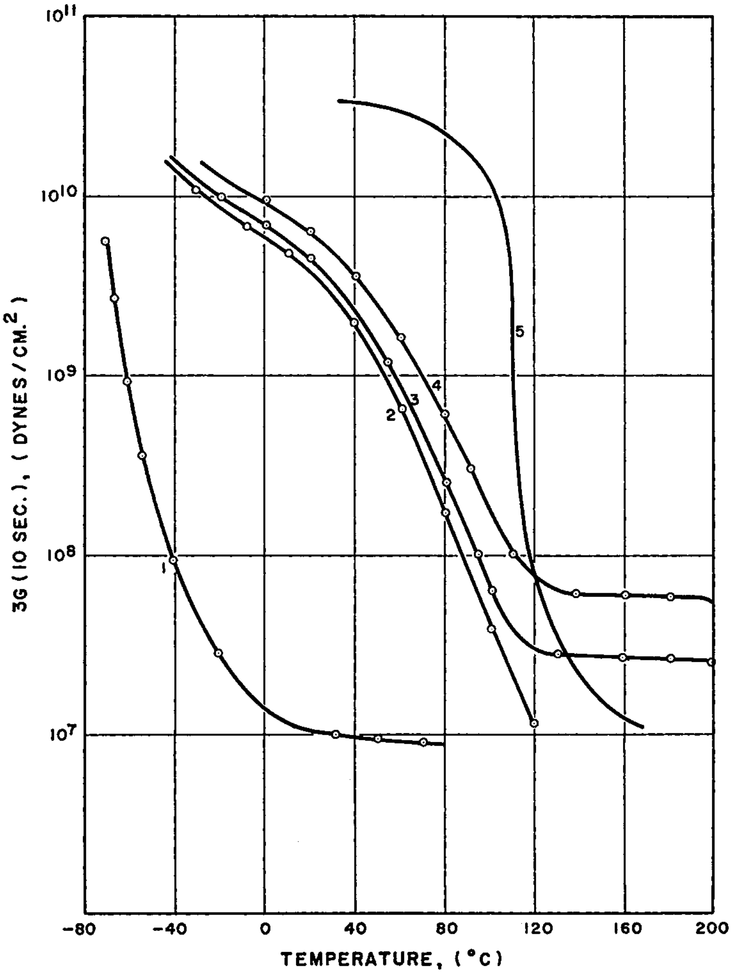


Fig. 3. Propylene oxide-methyl methacrylate block polymers. Percentage polyether prepolymer: (*1*) reacted with ethylenediamine; (*2*) 26.3%, methyl methacrylate 73.7%; (*3*) 26.3%, methyl methacrylate 73.7% +5% tetraethylene glycol dimethacrylate; (*4*) 26.3%, methyl methacrylate 73.7% +20% tetraethylene glycol dimethacrylate; (*5*) pure polymethyl methacrylate.

It is obvious from curve *C* in Figure 8 that after 24 hrs. the reaction was practically complete. A separate IR analysis over the 2–14 μ range revealed the presence of an isocyanate group in the product (absorption peak at 4.45 μ). The polypropylene oxide monoisocyanate (42%) reacted with *tert*-butyl hydroperoxide in the presence of styrene (58%), and the block polymer was isolated as described under Experimental. On the basis of the extinction coefficient at 13.5 μ (Fig. 9) the polystyrene content was found to equal to 57.8%. The presence of large amounts of polypropylene oxide is obvious from the high intensity of the peak at 9.1 μ (Fig. 9).

Evidence confirming block formation was obtained from the following experiments.

(*a*) Polypropylene oxide monoisocyanate reacting with *tert*-butyl hydroperoxide in the absence of styrene (but in a manner identical with that described for block formation, see Experimental) yielded a product which was completely soluble in methanol.

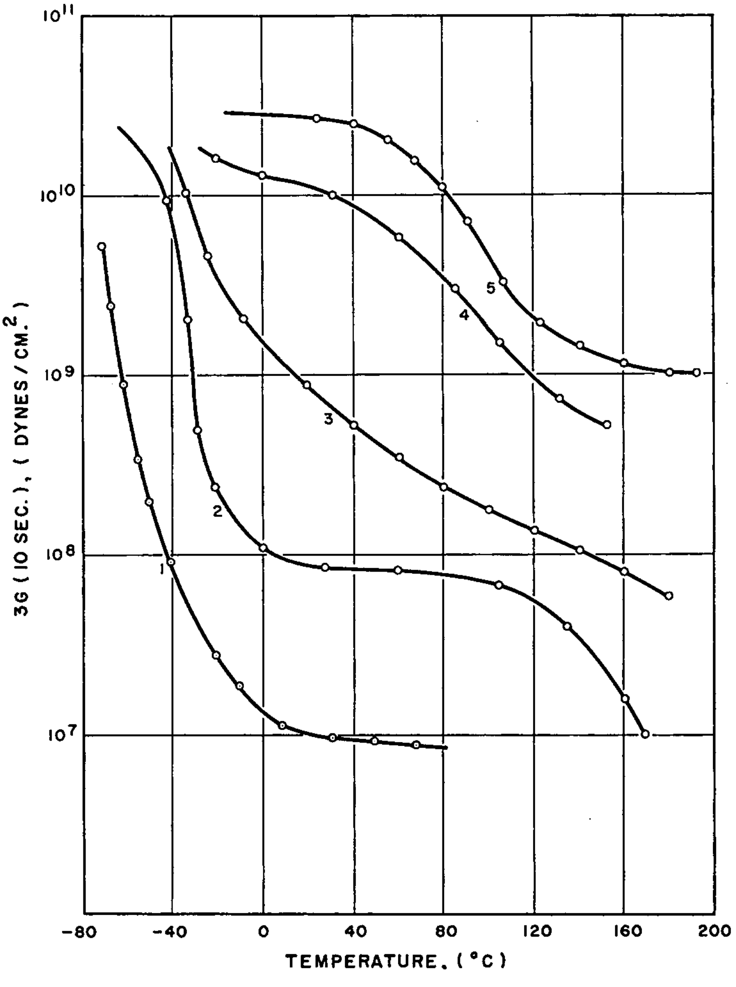


Fig. 4. Propylene oxide–acrylonitrile block polymers. Percentage polyether prepolymer: (*1*) reacted with ethylenediamine; (*2*) 81%, acrylonitrile 19%; (*3*) 50%, acrylonitrile 50%; (*4*) 21.6%, acrylonitrile 78.4%; (*5*) pure polyacrylonitrile.

(*b*) Exactly the same experiment was repeated in the presence of styrene and benzoyl peroxide (1%) and essentially pure polystyrene was isolated. The same experiment repeated with greater amounts of benzoyl peroxide (20%) yielded a solid and an oily layer.

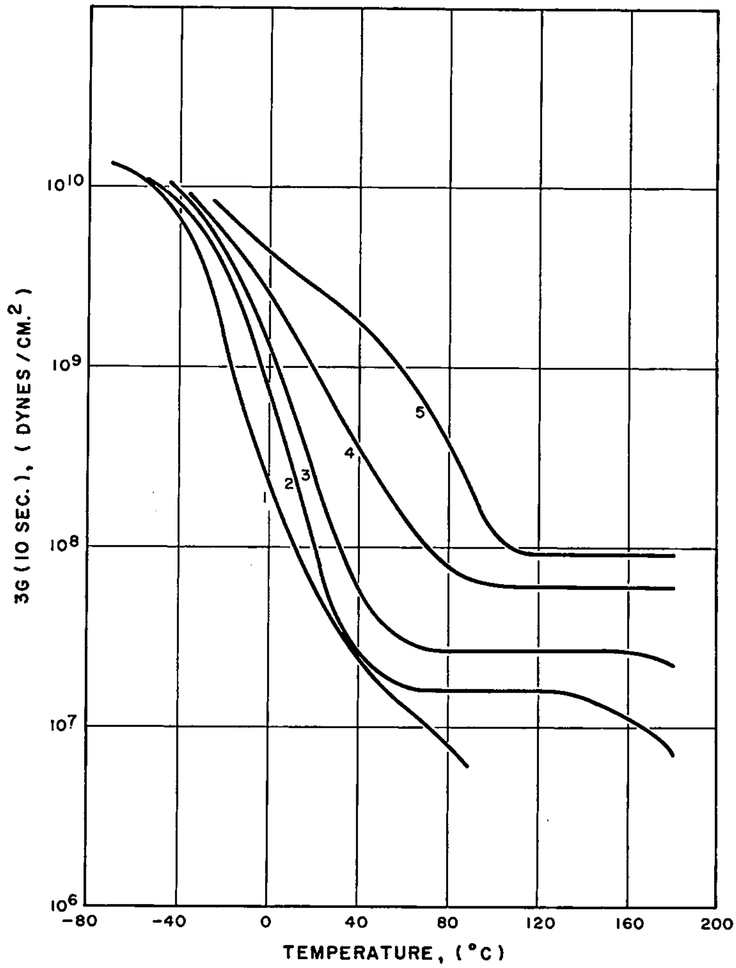


Fig. 5. Propylene oxide–styrene block polymers. Effect of crosslinking agent. Percentage polyether prepolymer: (*1*) 50%, styrene 50%; (*2*) 50%, styrene 50% + 2% tetraethylene glycol dimethacrylate (TEGDM); (*3*) 50%, styrene 50% + 10% TEGDM; (*4*) 50%, styrene 50% + 20% TEGDM; (*5*) 50%, styrene 50 + 30% TEGDM.

(*c*) Experiments similar to both (*a*) and (*b*), but with polypropylene oxide diisocyanate, yielded identical results.

(*d*) Precipitation of benzene-soluble blocks with methanol yielded stable, opaque, colloidal dispersions. This phenomenon previously was reported by several workers who synthesized graft polymers.[7,9–11] In the present case this result is due to the fact that part of the block polymer chain (polypropylene oxide) is soluble in methanol while part (polystyrene) is precipitated by methanol.

(*e*) Crystallinity of propylene oxide–polyacrylonitrile blocks was proved by taking x-ray diffraction patterns on films of pure polyacrylonitrile

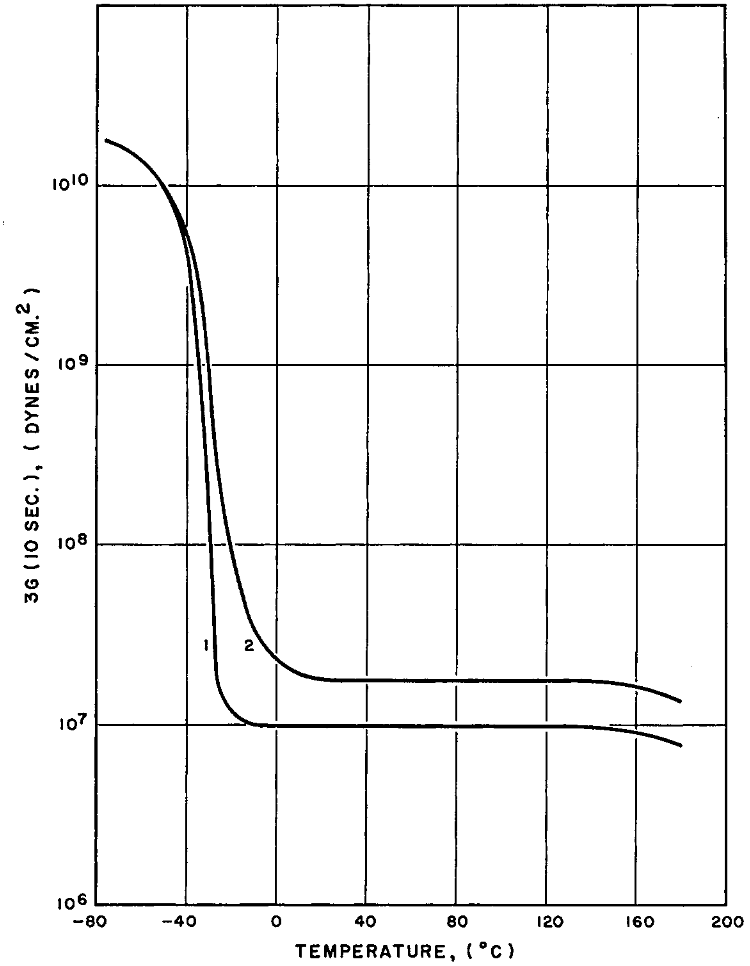


Fig. 6. Propylene oxide–*n*-butyl acrylate block polymers: (*1*) polyether prepolymer 50%, *n*-butyl acrylate 50% + 3.6% (*2*) polyether prepolymer 50%, *n*-butyl tetraethylene glycol dimethacrylate; acrylate 50% + 10.2% tetraethylene glycol dimethacrylate.

and blocks. The persistence of crystalline patterns is consistent with block formation.

(*f*) The IR spectrum of a block extracted with benzene (polyether 25%, polystyrene 75%) shows absorption peaks due to both components (Fig. 10).

The reactions of mono- and polyisocyanates were extensively studied and are the subject of two reviews.[12,13] It is will known that these compounds are extremely reactive and small variations in their structure or reaction conditions lead to different products. It was previously reported that 2,4-tolylene diisocyanate reacts explosively[14] with *tert*-butyl hydroperoxide. We have been able to carry out this reaction in the presence of styrene at 0°C. and have shown that polymerization of the latter occurs in these conditions (see Experimental). The IR analysis also indicated the presence of NH groups in the polystyrene. These results agree with previous findings of O'Brien and coworkers[15] who have shown that phenyl peroxycarbamate may be used to polymerize styrene, the initiator remaining incorporated in the polymer chains. On the other hand, the same authors obtained some evidence of the elimination of CO_2 from the polymeric chains. During the block polymer formation by our technique, evolution of gas was not observed, and weight losses after polymerization

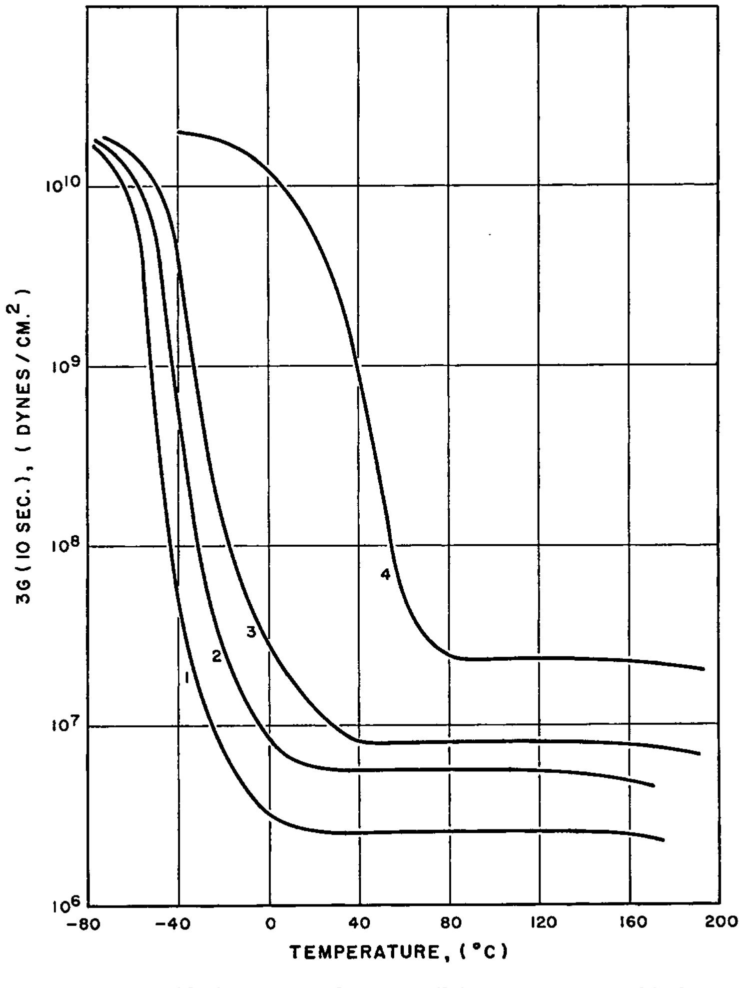


Fig. 7. Propylene oxide–isoprene and castor oil–isoprene, styrene block polymers: (*1*) polyether prepolymer 27.2%, isoprene 72.8%; (*2*) polyether prepolymer 76.0%, isoprene 24.0%; (*3*) castor oil triisocyanate 50%, isoprene 50%; (*4*) castor oil triisocyanate 39.3%, styrene 60.7%.

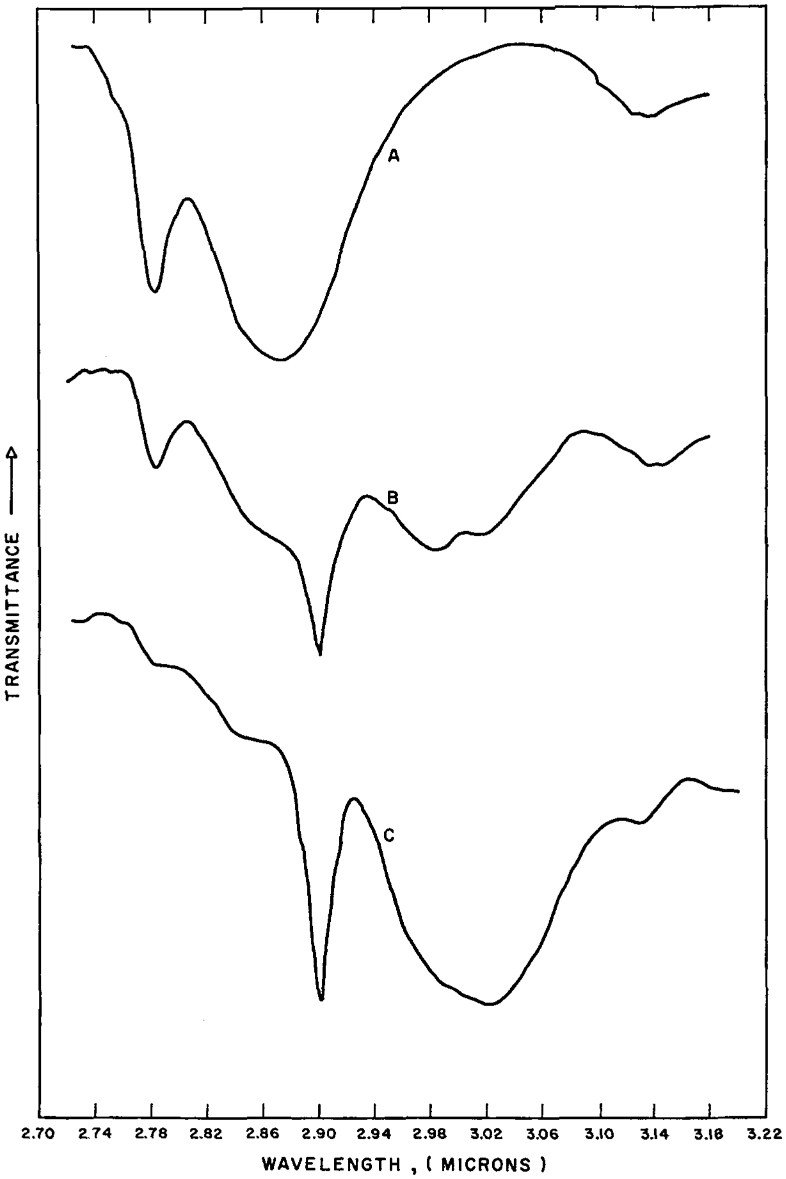


Fig. 8. Qualitative rate of formation of polypropylene oxide monoisocyanate; IR absorption spectrum (lithium fluoride optics): (*A*) polypropylene oxide with one hydroxyl group per chain; (*B*) the same reacted with 2.4-tolylene diisocyanate (after 5 hrs.); (*C*) the same, reacted with 2.4-tolylene diisocyanate (after 24 hr.).

also were too small to account for complete loss of CO_2. A long-chain diperoxycarbamate in the experimental conditions described here may therefore behave in a different manner. However, a more precise investigation is necessary to settle this point decisively. On the basis of

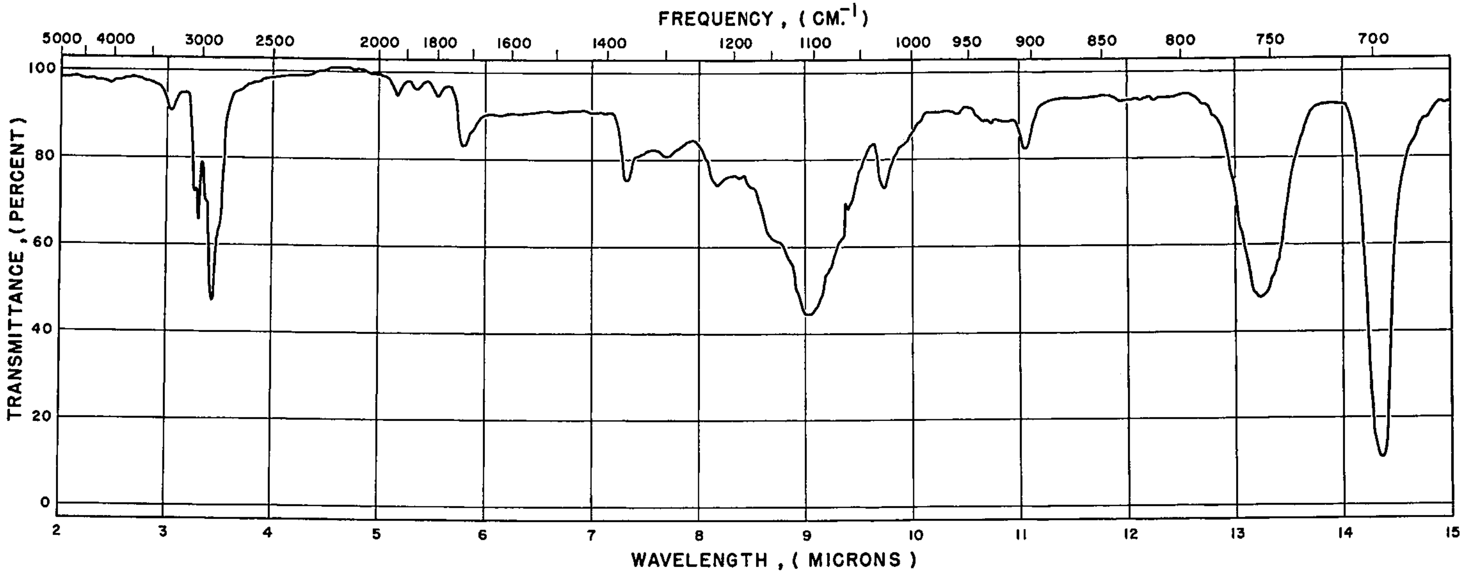


Fig. 9. IR spectrum of propylene oxide–styrene block polymer (solvent CS_2).

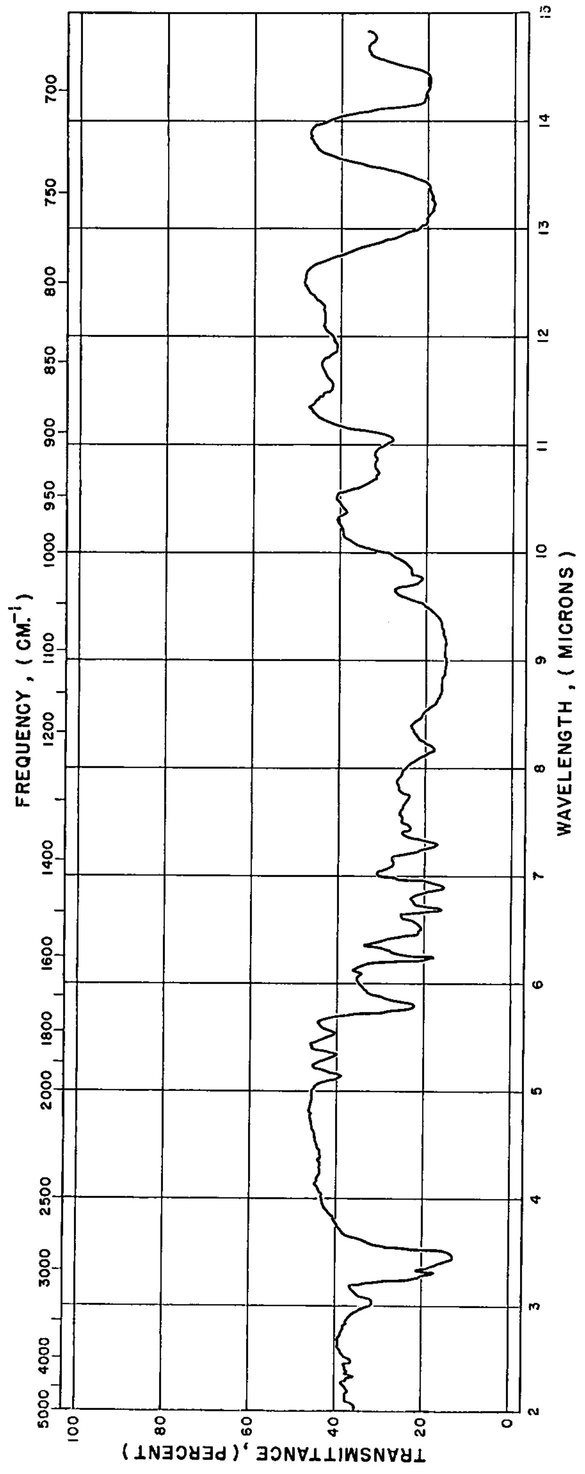
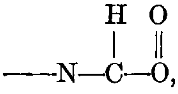


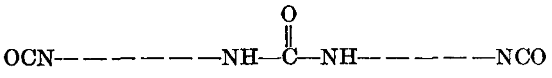
Fig. 10. IR spectrum of propylene oxide–styrene block polymer (film).

the experimental evidence thus far the following two predominant mechanisms may be postulated for our system:

(*1*) The reaction of a prepolymer terminated with two isocyanate functionalities in the presence of *tert*-butyl hydroperoxide and a vinyl monomer leads to block polymers through the formation of a diperoxycarbamate with subsequent breaking of the O—O bond and formation of the radical  $—\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}—\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}—\mathrm{O}$, which may form either a urethane or an NH link with the vinyl monomer.

(*2*) Alternatively, polymerization of the vinyl monomer by means of OH radicals originating from *tert*-butyl hydroperoxide decomposition may lead to OH-initiated chains, which would certainly react with isocyanate groups to yield blocks of a structure similar to, if not identical with, that indicated in the mechanism (*1*), above.

The first mechanism is supported by the finding that the block formation process may be carried out in two steps; i.e., the diisocyanate may react first with *tert*-butyl hydroperoxide, and the peroxycarbamate free of hydroperoxide may be used to initiate a vinyl monomer (Example 1, Experimental). In view of the fact that OH groups have been found, by IR analysis, in styrene polymerized by means of *tert*-butyl hydroperoxide, the second mechanism is possible. The rate of decomposition of *tert*-butyl hydroperoxide is likely, however, to be lower than its rate of reaction with isocyanate groups (in our experimental conditions). Also, on the basis of the CH content, molecular weight, and IR spectra of polystyrene obtained by *tert*-butyl hydroperoxide initiation, one may conclude that the concentration of OH-terminated polystyrene chains is too small for the second mechanism to operate to any considerable extent. Secondary reactions, including the biuret and allophanate reaction, are indubitably taking place and may be responsible for some degree of crosslinking. Diphenylurea has been reported to be a side product of the reaction between phenyl isocyanate and *tert*-butyl hydroperoxide.[16] In the process described here this type of reaction would yield by analogy a substituted urea of the following structure:



$$\mathrm{OCN}————————\mathrm{NH}—\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}—\mathrm{NH}———————\mathrm{NCO} \qquad (5)$$

Equation (5) contains free —NCO groups which are capable of reacting further with either *tert*-butyl hydroperoxide or with hydroxy-terminated polystyrenes. The final block polymer would have a considerably higher molecular weight than expected from the previously considered mechanism and may be the cause of limited solubility of the block polymers in common organic solvents.

Several qualifying remarks must be added to the above discussion. Even if the formation of peroxy carbamate terminated prepolymer were complete, the theoretical amount of homopolymer of the vinyl monomer that would be expected in the gross product is 25%. Furthermore, we have no proof that the conversion to peroxy carbamate is complete; under certain experimental conditions the conversions might be low. In these cases the proportion of homopolymers may be higher. Some products that we have prepared and whose mechanical properties we have illustrated in Figures 3 through 7 are, in general, polyblends of homopolymer and block polymer: the block polymer serves as an especially effective compatabilizing agent for the homopolymers.

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Résumé

Des "prépolymères" obtenables industriellement et contenant une ou plusieurs fonctions isocyanate par chaîne, donnaient par réaction avec l'hydroperoxyde de *t*-butyle des longues chaînes de peroxycarbamates. On a trouvé que ceux-ci étaient capables d'initier aussi bien la polymérisation de nombreux monomères vinyliques que de diènes donnant lieu ainsi à une nouvelle classe de polymères à blocs ayant des propriétés physiques très intéressantes. Des "prépolymères" polyéthers et polyesters contenant une, deux ou trois fonctions isocyanates furent liés chimiquement avec du polyacrylate de *n*-butyle, du polyacrylonitrile et du polyisoprène. La formation de polymères à blocs était pouvée par des méthodes à la fois physique et chimique. Leurs propriétés mécaniques étaient illustrées par des courbes module de torsion–température. On a examiné l'influence de la variation dans la composition du polymère et de l'agent de réticulation sur le module d'élasticité. On a également essayé de déterminer les mécanismes de réaction.

Zusammenfassung

Die Reaktion von technisch zugänglichen "Präpolymeren" mit einer oder mehreren Isocyanatgruppen pro Kette mit *t*-Butylhydroperoxyd ergab langkettige Peroxycarbamate. Diese waren fähig, die Polymerisation einer grossen Zahl von Vinylmonomeren und Dienen unter Bildung einer neuen Klasse von Blockpolymeren mit sehr interessanten physikalischen Eigenschaften anzuregen. Polyäther- und Polyesterpräpolymere mit einer, zwei und drei funktionellen Isocyanatgruppen wurden chemisch an Polystyrol, Polymethylmethacrylat, Po'-*n*-butylacrylat, Polyacrylnitril und Polyisopren gebunden. Die Bildung von Blockpolymeren wurde mit physikalischen und chemischen Metyoden bestätigt. Ihre mechanischen Eigenschaften wurden anhand von Torsionsmodul-Temperaturkurven gezeigt. Der Einfluss einer Variierung der Zusammensetzung und eines Vernetzers auf den Elastizitätsmodul wurde untersucht. Mögliche Reaktionsmechanismen werden diskutiert.

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