Rigid backbone polymers XXI: Stress–strain behaviour of uncrosslinked and of crosslinked rodlike polyisocyanates

Shaul M. Aharoni
Chemical Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960, *USA*

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INTRODUCTION

It has been observed recently[1-6] that the stress–strain curves of rodlike and a few not-so-rigid polymers show uniform extension in tensile tests. That is, no necking and significant fall in stress at yield were observed. Among the rodlike polymers, poly(n-alkylisocyanates) are prominent[1-4], while polyimides (Kapton H)[6], cellulose nitrate[5] and cellulose acetate[5] may be counted among the less rigid polymers. It was further observed that the tensile deformation is uniform[1], and that upon failure, the torn specimens relaxed back to their original shape and dimensions[7]. In the case of the polyisocyanates, the data of Haward *et al.*[1-3] indicate that mechanical parameters such as modulus[2] and yield stress[1-3], are remarkably insensitive[3] to changes in the molecular weight (or the corresponding intrinsic viscosity [η]) of a given polymer but are very sensitive[3] to the polymer composition as determined by the length of its n-alkyl sidechains. Our previous observations were in excellent agreement with Haward *et al.*[1-3]. In this report preliminary data will be presented expanding the observations to polyisocyanates with longer n-alkyl sidechains.

To the best of our knowledge there exists in the literature only one theoretical paper[8] treating an aspect of the mechanical behaviour of rodlike macromolecules in the condensed state, namely, their nonlinear elasticity. At present there is no theory to treat the mechanical behaviour of crosslinked rodlike macromolecules. In the case of polyisocyanates, such crosslinked rodlike macromolecules can be easily prepared. An example of such a preparation, and the stress–strain curves of the crosslinked and uncrosslinked polymers will be presented below.

EXPERIMENTAL

All polymers and most monomers were prepared as described in detail in ref 4. Crosslinkable polymers were prepared by mixing the desired ratios of monomers and then polymerizing. N.m.r. analyses indicated that the polymer composition is essentially that of the monomer feed. For the polymer whose stress–strain curve is given in this report, 1-decenylisocyanate and n-octylisocyanate monomers in a ratio of 1:3 were copolymerized. The intrinsic viscosity of the resulting polymer was 3.2 dl g^{-1}. In concentrated solution the polymer is liquid crystalline. In order to crosslink the polymer, a 5% w/v solution (isotropic) of the polymer in toluene was prepared. 1% benzoyl peroxide was added to the solution and dissolved at room temperature. The solution was heated to 80°C and kept constant for 4 h. The resulting gel was filtered and the toluene remaining in the gel replaced by methanol, upon which the gel collapsed. Mass balance indicated that practically all the copolyisocyanate remained in the gel phase. The dried gel appeared highly birefringent when observed under the microscope in cross polarized light. Immersion to equilibrium in toluene increased the volume of the gel to ~10–11 times its dry volume. Preparation of specimens for stress–strain studies was performed by allowing the crosslinking reaction to occur in solutions cast in shallow trays and allowing the solvent to evaporate uniformly once the reaction is terminated. Specimens are then punched out of the resulting films. The above procedure was repeated for various ratios of 1-decenyl- and octylisocyanate, and for 1-decenyl- and undecylisocyanate, yielding similar results with respect to the polymerization, crosslinking and stress–strain curves of the copolyisocyanates. All polymers in this study had an intrinsic viscosity of 3.2 ± 0.4 dl g^{-1}. For comparison of the mechanical behaviour, thick specimens were prepared from paraffin wax (Gulf Oil) Corp.) and were tested with the polyisocyanates. All specimens were allowed to reach constant weight before being subjected to the mechanical tests, indicating that no residual solvent remained in them.

Tensile tests were performed on an Instron instrument at 23°C and 50% relative humidity at a nominal strain rate of 8.3×10^4 s^{-1}. Intrinsic viscosities in toluene, n.m.r. analyses and cross polarized light microscopy, were performed as usual.

RESULTS

The investigated polymers were poly(n-butylisocyante), poly(n-hexylisocyanate), poly(n-octylisocyanate), poly(1-decenylisocyanate), poly(n-undecylisocyanate) the uncrosslinked and crosslinked forms of a 1:3 copolymer of 1-decenyl- and n-octylisocyanate, and paraffin wax as a model for poly(n-alkylisocyanates) with long sidechains. Stress–strain curves of each polymer are presented in *Figure 1*. These are typical of at least five such curves obtained for each. All the curves of poly(butylisocyanate) showed the indicated yield point followed by strain hardening and eventual failure at rather high strains. Qualitatively, we have observed that in the intrinsic viscosity range of [η] = 2–8 dl g^{-1}, the yield stress of poly(n-butylisocyanate) is very insensitive to the polymeric molecular weight, M. The ultimate strain and stress are, however, M-dependent, decreasing with M toward the yield stress. One specimen of poly(n-hexylisocyanate) showed a definite yield, closely followed by failure. The other specimens appeared as if they failed just prior to yield. All other polymers, with the exception of poly(n-undecylisocyanate) showed a smooth and moderate curvature to their stress–strain curves, somewhat reminiscent of elastomers at low elongations. The stress–strain curves of poly(n-undecylisocyanate) appeared as straight lines connecting the origin and the point of failure.

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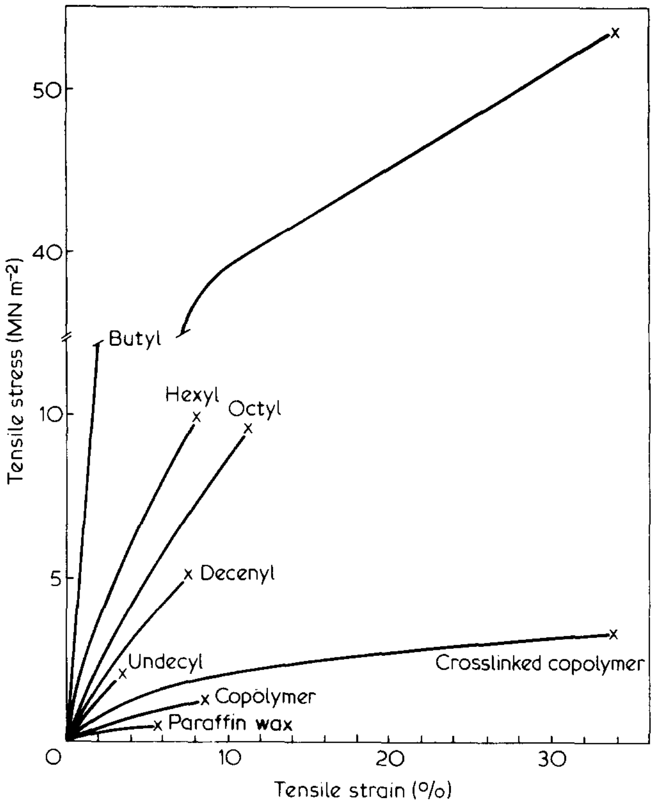

Figure 1 Tensile stress vs. tensile strain for the specified polyisocyanates and paraffin wax. Notice the change in scale of tensile stress. Strain rate = 8.3 x 10^{-4} s^{-1}; T = 23°C

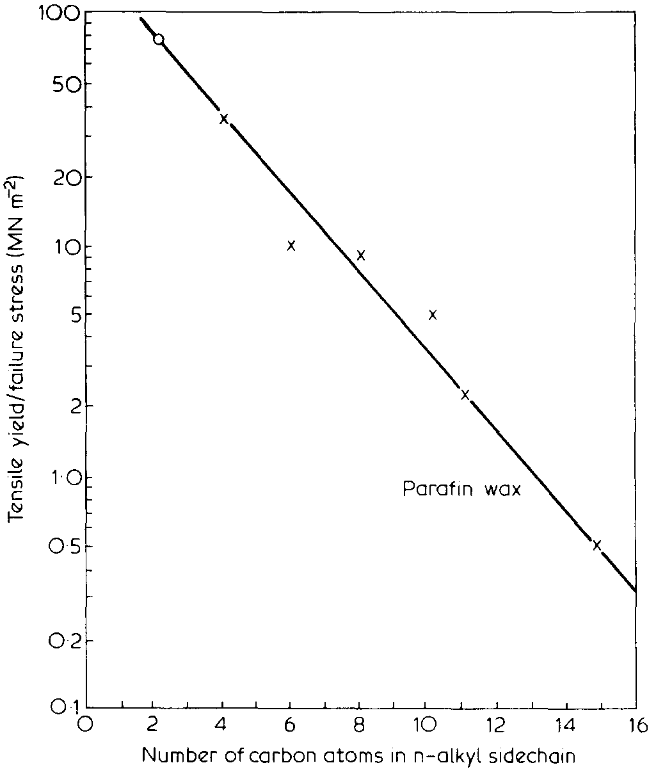

Figure 2 Tensile yield/failure stress plotted against the number of carbon atoms in n-alkyl sidechain of polyisocyanates

Because of the insensitivity of the yield stress to the molecular weight of polyisocyanates, and because all the polymers studied had rather close $[\eta]$ values, in the range of 3.2 ± 0.4 dl g^{-1}, it was felt that the tensile yield stress of poly(n-butylisocyanate) can be compared with the failure stresses of polymers that fail prior to yielding. The results are plotted in *Figure 2*, and appear to indicate an inverse logarithmic dependence of the respective stress on the number of carbon atoms in the n-alkyl sidechain of the polyisocyanates. The failure stress of paraffin wax falls in a position corresponding to a poly(n-alkylisocyanate) with 15 carbon atoms in the sidechain. In light of the fact that the sidechains of poly(n-alkylisocyanates) having 13 and more carbon atoms co-crystallize with each other[4] in a form similar to triclinic polyethylene[9], it appears that for such polymers the sidechain interactions are similar to the interactions between paraffin wax chains. Stress–strain data for poly(ethylisocyanate) are not available. Nevertheless, extrapolation of the data of ethylisocyanate-containing copolymers[1-3] leads to yield stresses of the order of 70–80 MN m^{-2}. This is indicated by an oval in *Figure 2*, through which the line passes. The stress–strain curves in *Figure 1* indicate that the tensile moduli of the investigated polyisocyanates decrease with increased sidechain length. One concludes that, in agreement with Haward *et al*[1-3], the tensile yield or failure stress and the tensile modulus are inversely dependent on the length of the sidechain.

The stress–strain curves of the uncrosslinked and crosslinked copolyisocyanate are shown in *Figure 1*. Neither shows a yield point, both being similar in overall shape. The curve of the crosslinked copolyisocyanate shows, however, a remarkable strain level at the point of failure, and somewhat higher stress at comparable strains. The improved performance of the crosslinked copolyisocyanate is due, we believe, to the crosslinks facilitating the distribution of stresses over the whole specimen and to the fact that the crosslinks prevent premature failure. The nature of the shape of the stress–strain curves of the polyisocyanates, and the similarity between the curves of the crosslinked and uncrosslinked copolymer, are not understood by us and their explanation will have to wait for future theoretical developments.

Stress–strain curves similar in nature to ours, were reported in the literature[10-12] for polyacrylates and polymethacrylates with long sidechains.

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