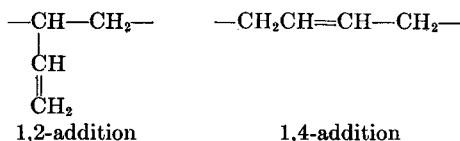


On the Presence of Crystallinity in Hydrogenated Polybutadienes

A low level of crystallinity in hydrogenated hydroxy-terminated polybutadiene (HHTPB) and in elastomers prepared from this prepolymer was surmised. However, no crystallinity could be detected by direct measurements such as x-rays or volume changes.^{1,2} This note discusses recent results of optical and rheological measurements which provide evidence for the presence of very small crystallites.

The HHTPB prepolymer (Telogen S, General Tire and Rubber Chemical Co., Akron, Ohio) was prepared by anionic techniques which lead to both 1,2- and 1,4-additions of butadiene:



Hydrogenation of the 1,4-chain leads to polyethylene, a highly crystalline polymer, whereas hydrogenation of the 1,2-chain would yield poly-1-butene, presumably atactic and hence noncrystalline. The prepolymer used for this study had 30 mole-% of 1,2-addition (i.e., 15% of backbone carbons), a quantity judged to be insufficient to prevent crystallization by analogy to the known behavior of ethylene-propylene copolymer. For the latter, a minimum of 18% of propylene is required in order to secure a noncrystalline rubber.

The evidence for crystallinity is based on the following observations. The prepolymer is a cloudy or translucent liquid that develops a grainy surface appearance as it is poured. These features are similar to those of solutions of low molecular weight cellulose triacetate and tributyrate, which are known to contain crystallites. As a simple, definitive test, the liquid was examined under polarized light, since crystallites will depolarize initially polarized light (the HHTPBD was a depolarizer). Moreover, by measuring the depolarization as a function of temperature, the melting temperature, i.e., the temperature at which depolarization ceased, was found to be $46 \pm 1^\circ\text{C}$.

As a check on this point, the viscosity of the prepolymer was measured as a function of temperature. The crystallites will increase the viscosity over that of a noncrystalline sample of the same molecular weight by acting as both fillers and chain extenders to produce a higher effective molecular weight. Near the melting point, there should be a rather sharp change in viscosity as the system reverts to a simple liquid. Figure 1 shows the results and indicates a melting point between 30° and 35°C . The lower apparent melting point is ascribed to the fact that the influence of the crystallites on viscosity will disappear before the last trace of crystallinity disappears. In both cases, the prepolymer remained clear for several hours after returning to room temperature.

Even though crystallinity is detected in the prepolymer, it may not carry over to the elastomer, since the chain extension and crosslinks could conceivably confer enough additional chain irregularity to prevent crystallization. Therefore, modulus-temperature studies were made on the elastomer, with results shown in Figure 2. The sharp dropoff at -50°C from about 10^{10} to 10^8 dynes/cm² is caused by the glass transition temperature T_g . At this point, the material is translucent. For materials known to be amorphous, such as polyisobutylene, the equilibrium modulus is reached shortly above T_g , whereas for partially crystalline materials, the modulus drops off gradually over a wide temperature range as more and more crystallites melt. For the HHTBP elastomer, the gradual modulus dropoff between -45° and $+45^\circ\text{C}$ strongly suggests crystallite melting, the process being completed at $+45^\circ\text{C}$, where the equilibrium rubbery modulus is attained. Throughout this temperature region, the modulus change is paralleled by an increase in transparency of the rubber, and the material becomes clear at $+45^\circ\text{C}$. Moreover, upon cooling below $+45^\circ\text{C}$, the equilibrium modulus is maintained down to room temperature. However, the modulus slowly increases on standing, as expected for a slowly crystallizing material.

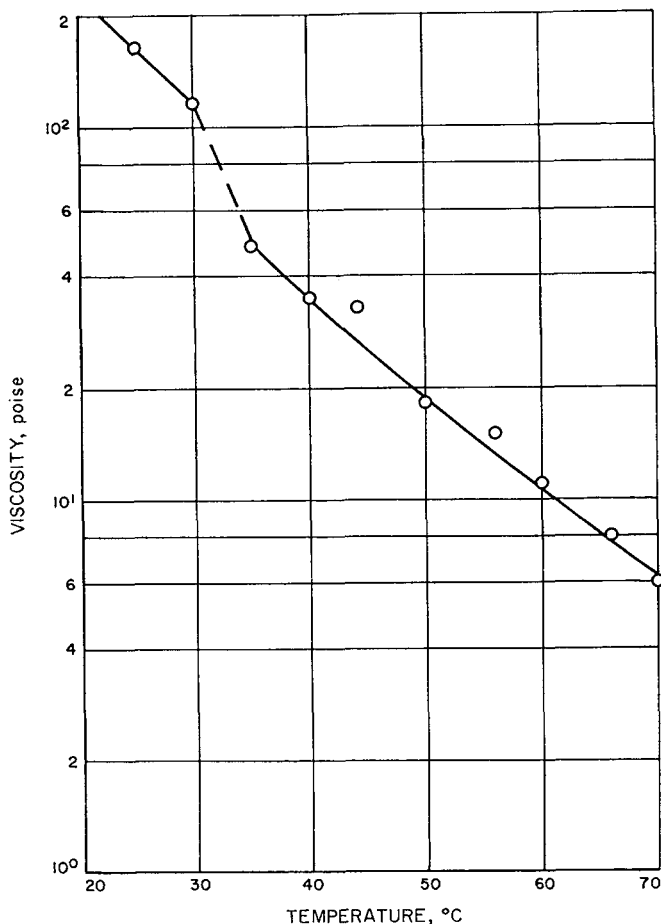


Fig. 1. Bulk viscosity for prepolymers.

Additional evidence is obtained from the study of the stress relaxation behavior (Fig 3). The curves for -14.5° , 1° , and 24°C are drastically different both in shape and relative position from those at 70° and 129°C . The last two curves are characteristic of noncrystalline crosslinked rubbery materials, i.e., the higher temperature curves exhibit a higher modulus (modulus $\sim T$), and the modulus changes only very slightly with time.

If the material were noncrystalline, the low temperature modulus curves should exhibit progressively lower values with decreasing temperature and the modulus should change only slightly with time, at least until the glass transition region is approached.

It is observed from Figure 2 that the transition is sharp, as indicated by the steepness of the curve at -50°C , so that at -14.5°C , in the time scale of the stress relaxation run, the rubbery region should have been reached. However, the modulus at -14.5°C is much higher than at 1°C , which in turn is higher than at 24°C and decreases with time more rapidly than at either 70° or 129°C . This indicates that crystallites are present, that they act normally in increasing the modulus of a material, and that they melt over a wide range in a manner characteristic of a material possessing a wide distribution of crystallite sizes. Also, it is apparent that time-temperature superposition could not be achieved with these curves.

It should be pointed out that crystallization of unreacted trimethylolpropane, the crosslinking agent, is possible. However, the presence of as much as 1 vol-% of crys-

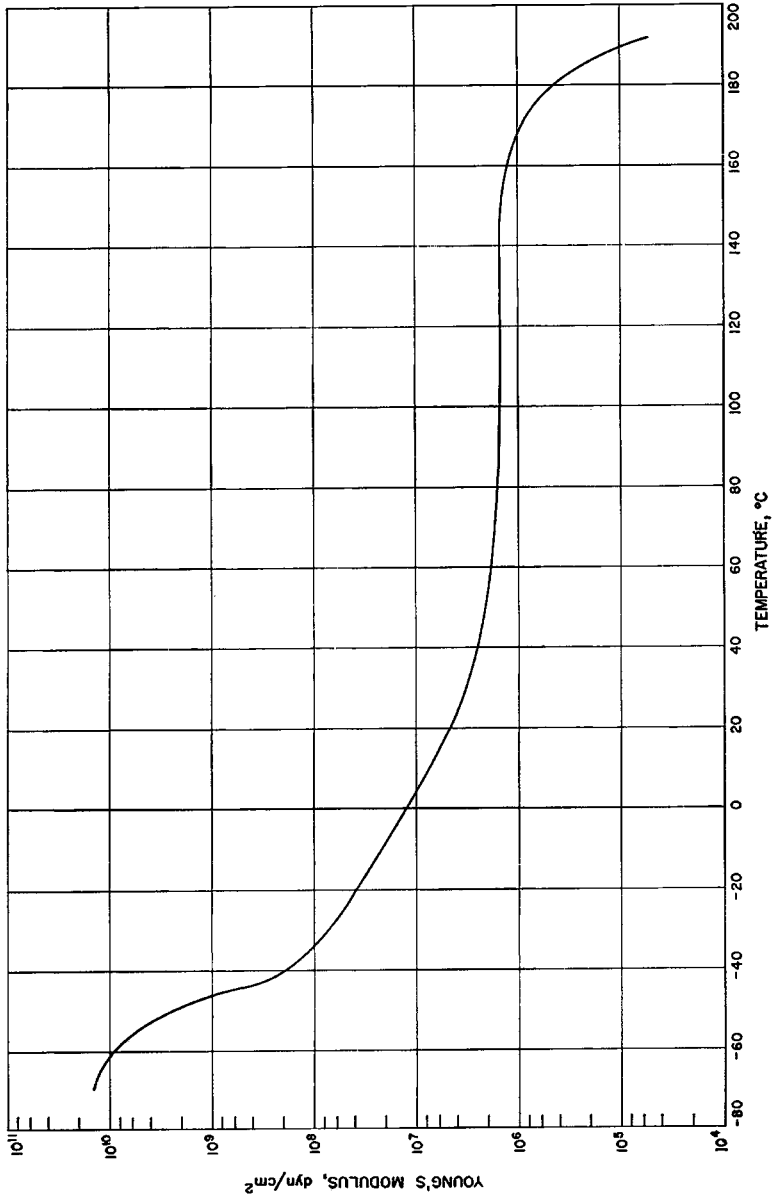


Fig. 2. Modulus curve of urethane elastomer prepared from Telogen S.

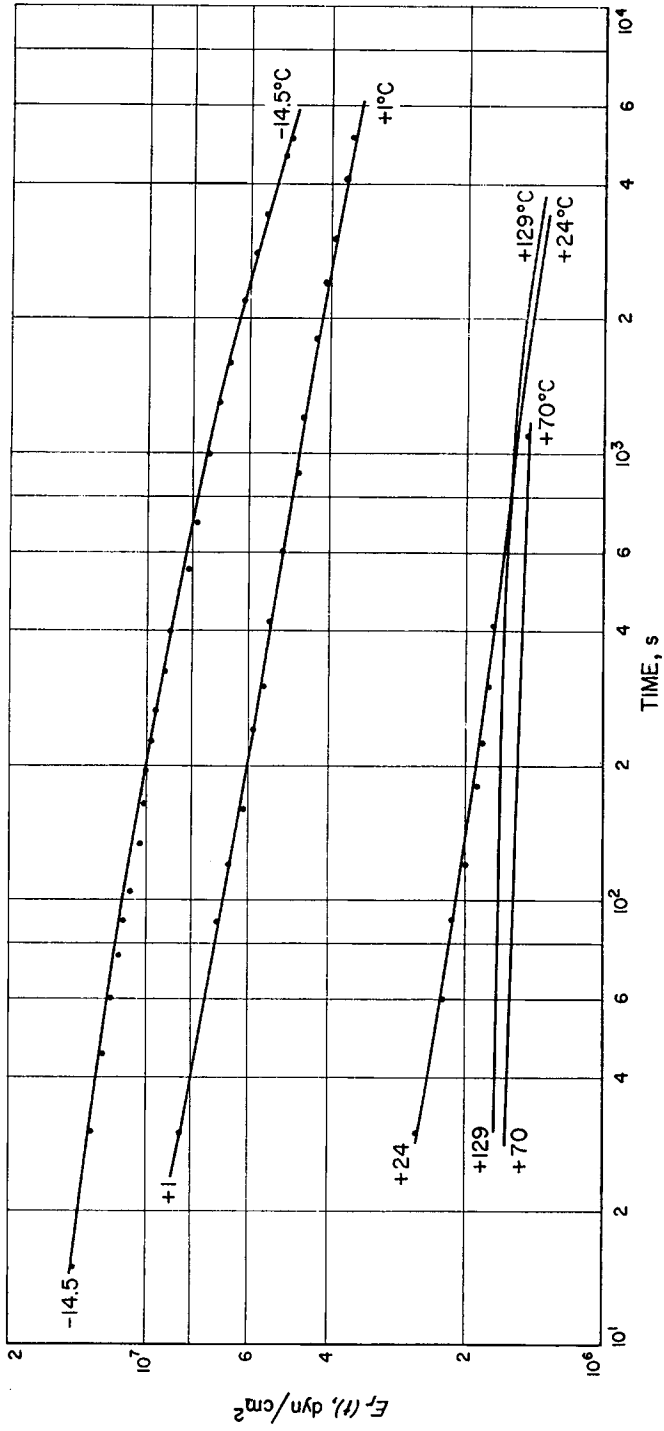


Fig. 3. Stress relaxation for elastomers.

talline filler would raise the modulus by about 2%,³ which certainly cannot explain the tenfold difference in modulus between +70° and -14.5°C.

The strongest evidence against crystallinity² is based on the absence of a crystalline x-ray diffraction pattern, and the absence of a melting transition from both dilatometric measurements and differential thermal analysis (DTA). It should be stressed that, in order to detect a transition, all these methods require the presence of an appreciable amount of crystallinity. For instance, the diffuse halo for the amorphous polymer may overshadow a weak crystalline x-ray pattern.⁴ Also, the increase in the specific volume upon melting poly(ethylene oxide), which is nearly 100% crystalline and has a sharp melting point, is only on the order of 8%. It follows that for 1-10% crystallinity, the volume change would be between 0.1% and 1.0%, and the melting would occur over a wide temperature interval. Dilatometry would then yield a minor change in slope, and DTA, a displacement of the baseline. Thus, if only a small amount of crystallinity is present, and the crystals present a wide distribution of size and a wide melting range, detection of crystallinity by these techniques becomes exceedingly difficult.

In conclusion, the evidence for the existence of crystallites can be summarized as follows:

1. The prepolymer depolarizes light, and this depolarization disappears at $46^\circ \pm 1^\circ\text{C}$ for the sample studied.
2. The viscosity-temperature curve for the prepolymer exhibits a discontinuity at about 35°C.
3. The modulus-temperature curve for the elastomer is characteristic of a material with a low content of crystallites of wide size distribution; the hysteresis effect reflects the low rate of crystallization.
4. The low crystallite content is consistent with the inability to detect melting by dilatometry, DTA, or x-rays.
5. The stress relaxation curves below 45°C are characteristic of crystalline polymers, whereas above 45°C a classical rubbery behavior is observed.

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