Poly(norbornene): Tensile and Dynamic-Mechanical Properties

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Synopsis

The tensile and dynamic mechanical properties of poly(norbornene), prepared through ring-opening polymerization, were studied. Tensile strength and extensibility increased, while Young's modulus decreased with increasing molecular weight and with increasing content of *trans* relative to *cis* unsaturation. The damping factor Δ was dependent on molecular weight only for the lower molecular weight samples. The out-of-phase modulus E'' and the damping factor decreased as the *trans/cis* ratio increased.

Poly(norbornene) represents a novel polymeric structure in which a five-membered ring is coupled to ethylenic unsaturation which may orient *cis* or *trans* with respect to olefinic hydrogens:



The synthesis of poly(norbornene) has been reported by several investigators. An all-trans polymer was synthesized¹ and so was an all-cis polymer.² Poly(norbornene) has also been made with varying amounts of cis and trans.^{3,4} Yet less has been reported on poly(norbornene) mechanical properties. The purpose of this work was to investigate the mechanical behavior of poly(norbornene) made by coordination polymerization^{3,5} in the range of intrinsic viscosity from 3 to 9 dl./g. (benzene, 30°C.) with varying contents of cis and trans unsaturation (the ratio of optical densities at 10.35 μ , trans, to optical density at 13.8 μ , cis, ranged from 3 to 4.3). Both tensile and dynamic properties were examined. A Vibrating Reed apparatus and a Torsional Pendulum instrument (Plas-Tech Co.) were used for dynamic measurements. Tensile measurements were made with an Instron Table Model machine connected to a highspeed recorder (Sanborn 301). Samples were cast from benzene solution and dried under vacuum.

Tensile strength and extensibility increased, but stiffness (Young's modulus) decreased with higher molecular weight and greater *trans/cis*

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ratio (Table I). From curves of the damping factor versus the temperature and of the in-phase modulus versus the temperature a transition was found at 50°C. This transition may be due to the five-membered ring structure. Although the damping capacity decreased with higher molecular weight



Fig. 2. Change in out-of-phase modulus E'' at 25°C.



Fig. 3. Effect of *cis* content on damping factor. Intrinsic viscosity: (1) 3.6; (2) 4.2; (3) 5.0; (4) 9.0.



Fig. 4. Change in out-of-phase modulus with *trans/cis* content .Intrinsic viscosity. (1) 3.6; (2) 4.1; (3) 5.0; (4) 9.0.

Mechanical Properties of Poly(norbornene)*				
Intrinsic viscosity, ^b dl./g.	3.4	4.3	5.0	9.0
trans/cis°	3	4	4.2	4.3
Tensile strength, psi	$3 imes 10^3$	$4.2 imes10^3$	$4.8 imes10^3$	$6.5 imes10^3$
Ult. elongation, %	16	80	85	300
Young's modulus, dynes/cm. ²	$9 imes 10^8$	$7 imes 10^8$	$5 imes 10^8$	$2 imes 10^8$

 TABLE I

 Mechanical Properties of Poly(norbornene)

* At strain rate of 100%/min. and 25°C.

^b In benzene at 30°C.

° Ratio of optical densities at 10.35 and 13.8 μ .

(Fig. 1), the damping factor Δ remained at a level indicative of superior impact resistance. The damping factor remained essentially constant at intrinsic viscosities greater than 6. The out-of-phase modulus E'' also decreased with higher intrinsic viscosity (Fig. 2). This reduction in E''could mean less intramolecular motion. The damping factor also dropped as the *trans/cis* ratio increased (Fig. 3). As the *cis* content decreased, the polymer became less rubberlike and more thermoplastic in nature. The out-of-phase modulus also was lowered with higher *trans/cis* content (Fig. 4). With lower *cis* content reduced intramolecular motion is indicated.

At the intrinsic-viscosity levels and *trans/cis* ratios investigated poly-(norbornene) appears to be a tough, flexible polymer with good impact resistance.

A model is proposed for the change in mechanical properties with greater molecular weight and *trans/cis* content, in which the close packing of polymer chains is altered. This causes less viscous resistance to distortion (greater extensibility and less stiffness). At the same time intramolecular motion is reduced at the carbon-to-carbon bonds (less energy loss [E'']/ cycle).

References

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