Solid State Properties of Poly(spiro[2,4]hepta-4,6-diene)

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ABSTRACT Poly(spiro[2,4]hepta-4,6-diene) (PSHD) is considered to behave like a rigid rod on the basis of the unusually large index ($\alpha=1.7$) in the viscosity-molecular weight relationship. Thus, some solid state properties were investigated with PSHD samples which contained different ratios of the 1,2- and 1,4-addition units. The thermo-mechanical curve of solvent-cast films showed that there were two $\tan \delta$ peaks below 300°C. The β peak was located at about 130°C (110 Hz), and affected little by the polymer composition. On the other hand, the position of the α peak shifted linearly from 200°C to 300°C with increasing fraction of the 1,4-unit, and the peak height decreased simultaneously. A loss peak associated with thermal decomposition and/or crosslinking was found at temperatures above 300°C. The TGA curve revealed that the thermal decomposition of PSHD takes place at about 300°C in air and at about 400°C under nitrogen. An exothermic peak was found in the same temperature range in the DSC curve. The crosslinked specimen showed no loss peak in dynamic measurements, which reflected immobilization of the molecule by crosslinks. The PSHD film did not show any indication of crystallinity.

KEY WORDS Poly(spiro[2,4]hepta-4,6-diene) / Rigid Polymer / Thermogravimetric Analysis / Thermomechanical Analysis / Viscoelastic Property /

One of the authors has reported that spiro[2,4]hepta-4,6-diene, a one-step derivative of cyclopentadiene, undergoes facile polymerization with a variety of cationic initiators.^{1,2} The polymer consisted of the 1,2- and 1,4-addition structures, as inferred from spectroscopic evidence. The cyclopropyl ring did not open during the course of the cationic propagation, in contrast with radical copolymerization.³

The content of the two structural units varied

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characteristically with counteranions when triphenylmethyl salts were employed as initiator.²

The relation between intrinsic viscosity and number-average molecular weight is represented by eq 2.

$$[\eta]_{\text{toluene}}^{30^\circ} = 4.5 \times 10^{-8} \cdot \bar{M}_n^{1.7} \text{ (dl/g)} \quad (2)$$

It is remarkable that the power index of $\bar{M}_n$ in the Mark-Houwink viscosity equation was 1.7, which is much greater than those of the usual flexible polymers with the random coil conformation. High index values such as this have been reported only for rodlike polymers like collagen and helical polypeptides.⁴ In fact, in the space-filling molecular model the spiro-cyclopropyl ring exerts large steric hindrance toward the conformational mobility.

In this paper, some solid state properties of this peculiar polymer are reported for the polymer samples of different structures. The effect of the polymer composition on the $\tan \delta$ peak in

the thermo-mechanical analysis was studied, and thermally-resistant properties produced by the molecular stiffness were measured by the TGA and DSC methods.

EXPERIMENTAL

Materials

SHD was prepared by a modification of the published procedure.³ A typical procedure is as follows. In a 500 ml three-necked flask equipped with a mechanical stirrer, a thermometer, and a graduated dropping funnel were placed 198 g (2 mol) of 1,2-dichloroethane, 320 g of 50-wt % aqueous sodium hydroxide (4 mol), and 4 g of trioctylmethylammonium chloride (phase transfer catalyst). The mixture was stirred at temperatures below 10°C, and cyclopentadiene (160 g, 2.4 mol) was added dropwise over 2 hr. Then the dropping funnel was replaced by a reflux condenser and the mixture was heated at about 60°C for 1 hr. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate overnight and distilled under reduced pressure. The synthetic yield of SHD was about 75%, as estimated by gas chromatography. The distillate containing unreacted 1,2-dichloroethane was purified by repeated distillations: bp 65°C (144 mm) [lit.⁵ 57°C (100 mmHg)]. The purity of the final fraction was better than 99%, as confirmed by gas chromatography.

Polymerization initiators and solvents, as listed in Table I, were prepared and/or purified by the previous methods.^{1,2}

Procedures

The polymerization of SHD was carried out

as follows. After flaming and cooling under reduced pressure, the polymerization flask was filled with dry nitrogen gas. Solvent and a catalyst solution were added through serum caps and the flask was cooled to about -76°C in a dry ice-methanol bath. Then a monomer solution was slowly added with stirring. The polymerization was stopped by adding a pyridine solution, and the polymer was recovered by pouring the reaction mixture into methanol.

PSHD films were cast from benzene solution and kept under reduced pressure for a week.

Instruments

Gas chromatograms were obtained with a Shimadzu GC-3AH instrument: Silicone GE SE31, 70°C, carrier gas H₂. Infrared and NMR spectra were obtained by using Perkin-Elmer Model 337 and JEOL Model JNM-MH60 spectrometers, respectively. Thermomechanical measurements were carried out with a Rheovibron dynamic viscoelastometer Model DDV-IIB; the frequencies employed were 3.5, 11, and 110 Hz. The heating rate was 1–2°C/min. Thermogravimetric analysis was carried out on a Cahn-RG-electrobalance, with a heating rate of 5°C/min. Differential scanning calorimetry was performed by a Rigaku Denki Thermoflex instrument. The heating rate was 5°C/min. X-ray diffraction was obtained by a Rigaku Denki Rota Unit RU-3.

RESULTS AND DISCUSSION

Polymerization

Table I gives the polymerization results. The polymerization was fast in all cases. The polymers obtained were soluble in many solvents, such as chloroform, benzene, toluene, 1,2-di-

Table I. Polymerization of SHD at -76°C

No.	Initiator, mmol/l	Monomer, mol/l	Solvent	Time, min	Con- version, %	$[\eta]_{\text{toluene}}^{30^\circ}$, dl/g	1,4-unit in polymer, %	
1	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	3.0	0.25	CH_2Cl_2	15	90	1.2	42
2	$\text{SnCl}_4\text{---TCA}^a$	0.25	0.25	CH_2Cl_2	10	90	3.0	38
3	$(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$	0.45	0.45	CH_2Cl_2	180	95	4.0	47
4	$(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$	0.13	0.30	$\text{CH}_2\text{Cl}_2\text{---toluene}$ (1 : 1)	10	90	4.8	70
5	$(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$	0.07	0.32	$\text{CH}_2\text{Cl}_2\text{---toluene}$ (3 : 7)	10	92	4.4	84

^a Trichloroacetic acid.

chloroethane, tetrachloroethylene, and carbon tetrachloride, and were white powders of fibrous materials. Intrinsic viscosities of 1.2 and 4.0 dl/g, for example, correspond to $\bar{M}_n=22,000$ and 47,000, respectively, based on eq. 2. The content of the 1,2- and 1,4-addition units was determined from the relative peak area of the olefin protons in NMR spectra, as described previously.² It is clear that the polymer structure can be varied extensively by changing the polymerization conditions.

X-Ray Diffraction

The X-ray diffraction pattern of PSHD cast films (samples: No. 1, 3, and 5 in Table I) showed halos in the cases of both the perpendicular and parallel irradiation of the X-ray beam to the surface of a film. Neither orientation nor crystallinity was detected for the roll-extended PSHD (room temperature, by a factor of two) and for the sample uniaxially drawn (220°C in a silicone oil bath, by a factor of five). The PSHD molecule is composed of two different structures. Presumably, the 1,2-unit will prevent straightening of rigid segments composed of the 1,4-unit sequence. The probable existence of *cis* and *trans* linkages between the structural units makes the situation more complex. These irregularities must interfere with the crystallization of PHSD.

Thermal Properties

Differential scanning calorimetry (DSC) curves of the polymer (sample: Table I, No. 1) are shown in Figure 1. The curve obtained under nitrogen atmosphere showed a slight shift of the base line to the endothermic side (downward) at about 190°C, while that in air (broken line) showed a deviation upward from the base line at the same temperature range. Consequently, the PSHD molecule appears to gain some molecular motions at temperatures above 190°C. The exothermic peaks at 351°C under nitrogen and at 362°C in air might be due to the decomposition reaction and/or crosslinking.

Figure 2 shows thermogravimetric analysis (TGA) curves under nitrogen gas (solid line) and in air (broken line). The oxidation of the polymer seems to take place at about 150°C, as reflected by a slight increase in the sample weight. The $\nu_{C=O}$ band (1,700 cm^{-1}) and the

Figure 1. DSC curves of PSHD in N_2 atmosphere (solid line) and in air (broken line): Sample, No. 1 in Table I.

Figure 2. TGA curves of PSHD in N_2 atmosphere (solid line) and in air (broken line): Sample, No. 1 in Table I.

ν_{OH} band (3,580 cm^{-1}) were newly observed in IR spectra of the sample annealed at 200°C. The decomposition was extensive above 300°C. The organic residue remained even above 500°C under nitrogen atmosphere, whereas no residue was found in air at the same temperature.

Dynamic Viscoelasticity

Figure 3 shows the temperature dependence of the mechanical loss tangent, $\tan \delta$, of PSHD (Sample: Table I, No. 1 and No. 5) measured at 110 Hz. There was no peak from -160 to $+100^\circ\text{C}$. The peaks were observed at 133°C (β peak), 246°C (α peak), and 335°C (decomposition peak). The PSHD sample with a higher 1,4-unit content (84%, Sample No. 5) gave a

Figure 3. $\tan \delta$ vs. temperature for PSHD samples: (○) 42.2% of the 1,4-units (sample, No. 1); (●) 84.3% of the 1,4-units (sample, No. 5).

Figure 4. Transition map of α and β dispersions ($\log f_{\max}$ vs $1/T$): Sample, No. 2 (●, ○); No. 3 (○, ●).

smaller $\tan \delta$ value above 170°C, and the α peak shifted to the higher temperature side when compared with the sample with lower 1,4-unit content (42%, sample No. 1). This difference may be explained by assuming that the sequence of the 1,4-unit is more rigid than that of the 1,2-unit and that the increase in the former unit suppresses the motion of molecular chains to a large extent. It is suspected that the stiffness of the PSHD molecule is mainly governed by the 1,4-structure.

Figure 4 shows the transition map of the α and β peaks, which was prepared by changing the measuring frequency. The mean activation energy of the α peak is 86 kcal/mol and that of the β peak is 30 kcal/mol for both samples.

First the value of activation energy of the α peak is estimated based on the WLF equation, which has been shown to be widely applicable to the glass-forming flexible molecules. The WLF equation is given by⁶

$$\log a_T = -c_1^g(T - T_g)/(c_2^g + T - T_g) \quad (3)$$

where a_T is the shift factor when T_g is taken as the reference temperature and c_1^g and c_2^g are constants characteristic of the polymer species. In the conventional expression, $c_1^g = 17.44$ and $c_2^g = 51.6$ are employed as the general values applicable to all kinds of polymers forming glassy states.

The activation energy for relaxation at any temperature T above T_g , ΔH_a , is evaluated by differentiating eq 3 with respect to the reciprocal temperature as follows:

$$\Delta H_a = 2.303 R c_1^g c_2^g T^2 / (c_2^g + T - T_g)^2 \quad (4)$$

If we assume that T_g of PSHD corresponds to the temperature at which the $\tan \delta$ curve deviates from the background, ΔH_a of the α peak at its peak temperature is evaluated by eq 4. The method for determining T_g was described first by Hideshima *et al.*,⁷ and is conveniently used for PSHD samples with various copolymer compositions. Its principle is based on the assumption that the beginning of any thermal motion associated with the micro-Brownian movement is reflected in the rise of the $\tan \delta$ curve of the α peak. For example, the α peak temperature and the T_g value are read from the $\tan \delta$ curve of Sample No. 5 in Figure 3 as 270°C and 200°C, respectively. Substitution of these values into eq 4. results in $\Delta H_a(250^\circ\text{C}) = 70$ kcal/mol. This value is smaller than the observed value of 86 kcal/mol but not inconceivable according to the WLF equation, especially when T_g is determined by the above method.

The basic assumption of the WLF equation is that the increase in the free volume fraction and the conformational change of the main chain take place by thermal activation. In the case of the PSHD chain, however, such conformational change is difficult to assume, as far as space-filling model can suggest.

Another possible interpretation of the molecular process of the α peak is the torsional oscillatory motion around the molecular axis. Such

Figure 5. Temperature for $\tan \delta$ maximum (110 Hz) vs. fraction of the 1,4-unit.

a mechanism was assigned by Yamafuji, *et al.*⁸ to the β relaxation of the polymers having no side chains such as poly(vinyl chloride), poly(ethylene terephthalate), etc. There will be various modes of the oscillatory motion around the chain axis. The lower modes of motion are considered to be influential along some lengths of the main chain which include several monomeric units. In other words, the α peak temperature and its relaxation magnitude are affected by the copolymer composition. This expectation is supported by the results in Figure 5.

Figure 5 shows the relationship between the α peak temperature in the $\tan \delta$ curve and the fraction of the 1,4-units in the polymer. The linear relation determined by the least squares method is given by eq 5:

$$T_{\tan \delta, \max} (^{\circ}\text{C}) = 1.03F + 197 \quad (5)$$

where F denotes the percent fraction of the 1,4-units. Using this equation, the temperature of the $\tan \delta$ peak for PSHD with 100% 1,4-units is evaluated as 300°C for the α peak. The polymer with 100% 1,4-units might crystallize and become more heat-resistant. The decrease in the intensity of the α -peak at higher 1,4-unit contents, as seen in Figure 3, will also produce better heat resistance.

The activation energy of the β peak (30 kcal/mol) is higher than those of the subpeaks of the usual vinyl polymers (10–20 kcal/mol).⁹ This difference is not unreasonable when it is taken into account that the β peak temperature

of PSHD is located at a temperature higher than those of other polymers. On the other hand, the nature of the β peak seems to be attributable to the local relaxation mode of the main chain associated with sequence shorter than that associated with the α peak. A more definite conclusion can only be presented after detailed studies on the stereoisomerism are performed. At present the following facts are available for discussing the nature of the β peak.

As seen in the thermomechanical curves of Figure 3, the β peak temperature and its relaxation magnitude are not sensitive to the copolymer composition or the difference in the main-chain configuration. When the sample was exposed to benzene vapor, there was no change in the magnitude of the β peak. Therefore, this peak is conceivably governed by the intramolecular factor. Soaking of the sample in sulfuric acid produced crosslinking, but the β peak was observed at almost the same temperature. This suggests that the molecular motion associated with the β peak is confined within a very limited range of the molecule.

The PSHD film (No. 1) turned bright black, probably due to development of the conjugated olefin system, when it was subjected to heat treatment up to 360°C. The α and β peaks disappeared almost completely after the heat treatment.

Figure 6 shows the storage modulus (E') curve and the loss modulus (E'') curve for PSHD

Figure 6. Temperature dependence of E' and E'' after heat treatment up to 360°C (●) and for the original sample (○).

samples before and after the heat treatment. The storage modulus varied little above 300°C for the heat-treated sample. This means that the thermal oxidation and intermolecular crosslinking inhibit every molecular motion. Consequently, a peak at 335°C in the $\tan \delta$ -temperature curve of the original sample is assigned to the initiation of such a crosslinking reaction. This temperature corresponds to the peak located at 350°C in the DSC curve. The progress of the crosslinking reaction was reflected in the rise of the modulus curve above 300°C, as seen in Figure 6.

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