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Synthesis and Characterization of Poly-[2-methoxy-4,6-di (2,7-Naphthyloxy)-s-triazine]

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ABSTRACT

Poly[2-methoxy-4,6-di (2,7-naphthyloxy)-s-triazine] was synthesized by interfacial polycondensation of 2-methoxy-4,6-dichloro-s-triazine with 2,7-dihydroxy-naphthalene. The polymer was characterized by IR and UV spectra, dynamic mechanical analysis, differential scanning calorimetry, and thermogravimetric analysis. The polymer was fractionated by the fractional precipitation method and the fractions were characterized by viscometry and membrane osmometry. The polymer has a T_g of 175°C and is found to be stable up to 300°C in air. The polymer sample is found to degrade in air in two steps, and the energy of activation for the first step is around 25 kcal/mol.

INTRODUCTION

Polycyanurates derived from 2-R-4,6-dichloro-s-triazine and aromatic diols have gained importance in the field of thermally stable polymers [1-8]. High temperature or melt condensation techniques lead to low molecular weight polycyanurates unsuitable for film or

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fiber formation; only the interfacial technique is reported to yield polymer samples of high molecular weight [1-9].

In the present communication, the synthesis of poly[2-methoxy-4,6-di (2,7-naphthyloxy)-2-triazine] (PMDNT) and its characterization are reported. The structural features of the PMDNT are supported by the results of IR and UV spectral studies. The polymer sample was characterized by differential scanning calorimetry and thermogravimetry. The dynamic mechanical properties of the polymer sample were also studied. The polymer sample was fractionated into five fractions by the fractional precipitation method, and the fractions were characterized by viscometry and membrane osmometry. The Mark-Houwink-Kuhn-Sakurada (MHKS) relationship was established.

EXPERIMENTAL

2-Methoxy-4,6-dichloro-s-triazine (MDT) (mp 90°C) was synthesized by a reported method [10]. 2,7-Dihydroxynaphthalene (mp 186°C) was crystallized from water. The solvents used were purified by fractional distillation.

Polymer Synthesis by Interfacial Polycondensation

In order to determine a suitable solvent for interfacial polycondensation, it was carried out using nitrobenzene, benzene, and chloroform as the solvents. Chloroform was found to be the best solvent for the purpose.

A solution of 2,7-dihydroxynaphthalene (4.05 g, 0.025 mol), sodium hydroxide (2 g, 0.05 mol), and cetyl dimethyl benzyl ammonium chloride (0.625 g) in 250 mL water was stirred vigorously at 15°C. To this solution a solution of MDT (4.5 g, 0.025 mol) in chloroform (65 mL) was added rapidly. The emulsion was stirred vigorously for 5 h. The contents were transferred to a separating funnel and the organic layer was separated, washed with water, and run into an excess of acetone to precipitate the polymer. The solid was filtered, washed well with water, and then with acetone. It was purified by dissolving it in chloroform and precipitating with methanol. The yield was 75%. It is soluble in chloroform, methylene chloride, and 1,2-dichloroethane. It formed tough and clear film when cast from polymer solution in chloroform.

The polymer, PMDNT, was fractionated by fractional precipitation using a 1% solution of the polymer sample in 1,2-dichloroethane and methanol as a nonsolvent. The fractionation was carried out at 30 ± 0.1°C. A standard procedure was adopted to accomplish this.

MEASUREMENTS

The IR spectrum was recorded with a Beckman IR-5 spectrometer using a thin film sample. The UV spectrum was recorded with a Specord UV VIS (Carl Zeiss Jena) model using a 10^{-5} M chloroform solution. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in air using a Du Pont 900 Differential Scanning Calorimeter and a Linseis Thermobalance, respectively, at a heating rate of 10°C/min. Dynamic mechanical testing on the film of PMDNT was carried out using a Du Pont 981 Dynamic Mechanical Analyser (DMA). The film was cast from a polymer solution in chloroform (5% w/v). The film was finally dried at 130°C under vacuum for 7 d.

Viscosity measurements on PMDNT fractions were carried out in chloroform at 35 ± 0.1°C with an Ubbelohde suspended level-type viscometer. The concentration of polymer solution used for the viscometric study ranged from 0.2 to 0.5 g/dL. The intrinsic viscosity $[\eta]$ was determined from the plot of η_{sp}/c versus c and also from the plot of $(\ln \eta_r)/c$ versus c. The number-average molecular weight ($\overline{M}_n$) of each fraction was determined in 1,2-dichloroethane at 25°C with a Hewlett Packard High Speed Membrane Osmometer - 502. $\overline{M}_n$ was estimated by the usual method.

RESULTS AND DISCUSSION

The polymer PMDNT is a grayish powder, soluble in aliphatic chlorinated hydrocarbons such as chloroform, methylene chloride, and 1,2-dichloroethane, but insoluble in alcohols, ketones, and DMF.

The reduced viscosities of the polymer samples prepared using different interface systems are shown in Table 1. When benzene is used as an immiscible solvent, the reduced viscosity, which can be taken as a measure of the order of molecular weight of the granular product, is very low. When nitrobenzene is used as an immiscible component, the polymer has a comparatively higher reduced viscosity but the polymer forms a brittle film. It may be noted that nitrobenzene is a poor solvent for the polymer. When chloroform was used as an immiscible solvent, a high molecular weight polymer yielding tough film was formed. Thus chloroform proved to be the best among the three solvents for interfacial polycondensation. The benefit of employing a good polymer solvent is presumed to result from the mobility of the polymerizing mixture and the continuing contact of MDT and phenoxide groups near the interface. It was also noted that only in the presence of a cationic emul-

TABLE 1. Conditions for the Interfacial Polycondensation of MDT with 2,7-Dihydroxynaphthalene and Reduced Viscosity of the Resultant Polycyanurate. Reaction Temperature: 15-17°C

Interface system	Time (h)	η_{sp}/c^a (dL/g)
Benzene-water	5	0.06
Nitrobenzene-water	5	0.10
Chloroform-water	5	0.40

[a] Solvent, chloroform; 30°C.

sifier was a high molecular weight, tough, film-forming polymer obtained. Hence, a cationic emulsifier was used for the synthesis. The cation of the emulsifier is presumed to be the effective agent and to form an adduct with the phenoxide which is more soluble in the organic phase than is the phenoxide. Thus contact with MDT in the organic phase is promoted and the polymerization rate is increased. The byproduct salt is then extracted by the aqueous phase and the cation is free to follow the cycle again [11]. The effectiveness of the cationic emulsifier has been found to depend on the nature of the solvent. The PMDNT synthesized under the optimum conditions had $[\eta] = 0.35$ dL/g in chloroform at 30°C.

IR and UV spectra of PMDNT are shown in Figs. 1 and 2. The IR spectrum showed strong absorption bands in the regions 7.2-7.3 and 8.2, 6-7, and 12.2 μm, typical of vibrations involving aryl-ether linkage, in-plane, and out-of-plane motion of the triazine ring system, respectively [2, 8, 12].

The DSC thermogram of PMDNT is shown in Fig. 3. It shows an endotherm in the 150-190°C region and an exotherm in the 225-270°C region. The glass transition temperature (T_g) was taken as the midpoint of the extrapolated pretransition and posttransition base lines as recommended by Brennan [13]. This procedure is reported to give reproducible results [14]. The exotherm may be due to crystallization in the polymer sample. Such an exotherm has also been observed in the DSC of a polymer prepared from MDT and bisphenol A [15].

The thermogravimetric curve for PMDNT is shown in Fig. 4. The sample starts decomposing in air above 300°C. Comparison of TGA with DSC provides a fair indication that the exotherm observed in DSC is due to crystallization since no weight loss is observed in TGA in that temperature range. The TGA of PMDNT shows two distinct degradation steps. Weight losses in the temperature ranges 325-400 and 525-650°C are fairly rapid and indicative of the complex nature of the degradation of the polymer sample. The TGA data were treated according to the Broido method [16] to estimate the activation energy in-

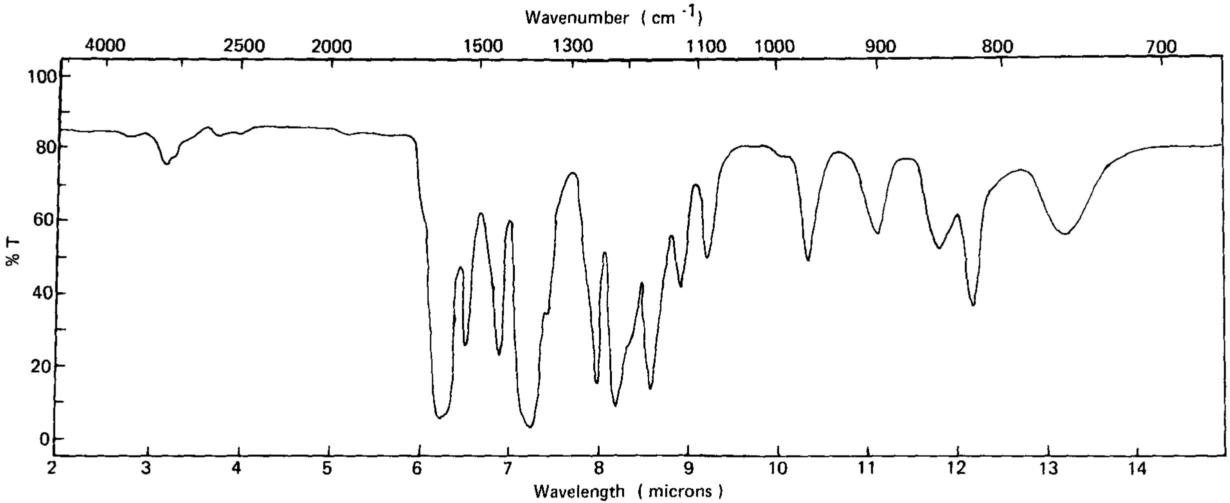

FIG. 1. IR spectrum of PMDNT film sample.

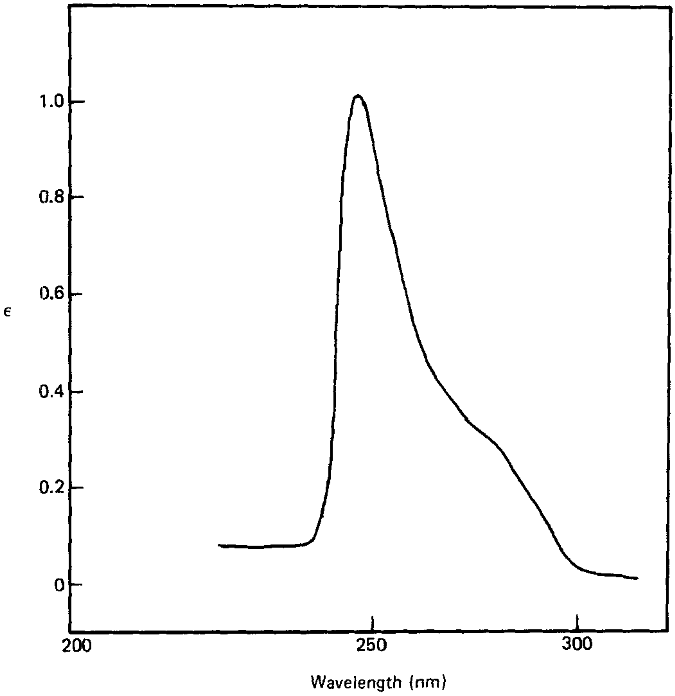

FIG. 2. UV spectrum of PMDNT.

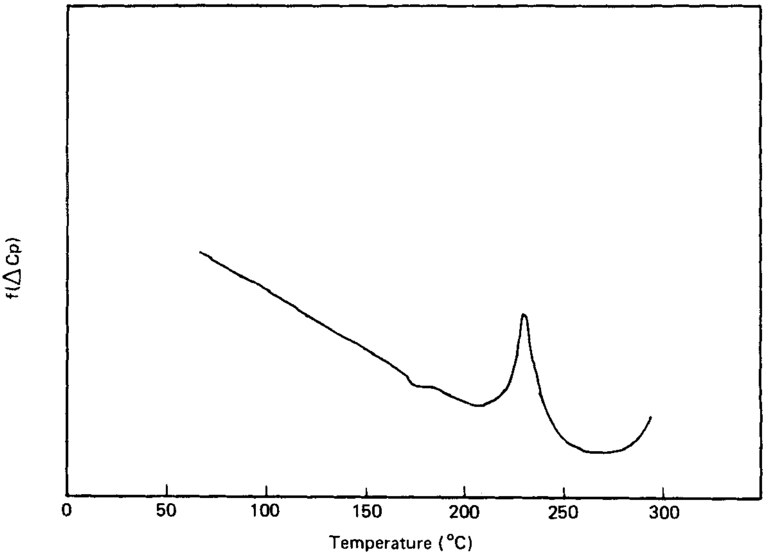

FIG. 3. DSC thermogram of PMDNT in air at 10°C/min heating rate.

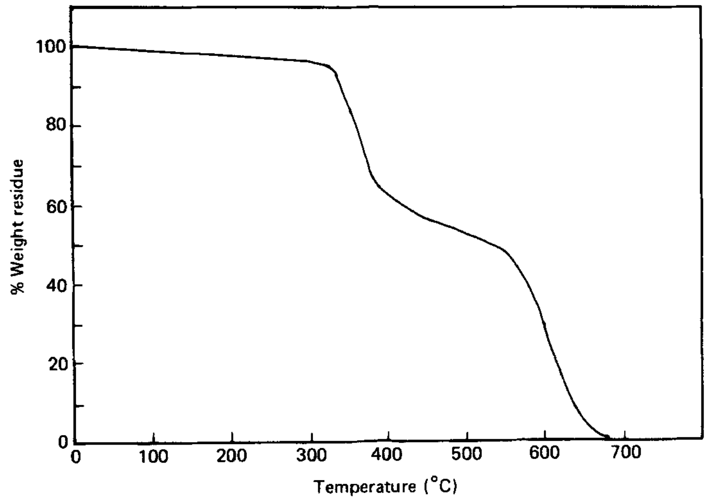

FIG. 4. TG thermogram of PMDNT in air at 10°C/min heating rate.

volved in the two degradation steps. Activation energy E for the first step is found to be around 25 kcal/mol and that for the second one around 27 kcal/mol.

The resonant frequency experimentally obtained from dynamic mechanical analysis (DMA) was converted to Young's modulus E for the sample by using the following equation (for a rectangular sample):

$$E\ (\mathrm{N/m^2\ or\ Pa}) = \left[\frac{(4\pi^2 f^2 J - K)}{2W(\frac{L}{2} + D)^2}\left(\frac{L}{T}\right)^3\right]\left[1 + 0.71\left(\frac{2T}{L}\right)^2 - 0.1\left(\frac{2T}{L}\right)^3\right]$$

where f = DMA resonant frequency (Hz)
J = moment of inertia of arm (1.554×10^{-3} kg·m^2)
K = spring constant of pivot (0.356 Nm/rad)
D = sample clamping distance (9.6×10^{-3} m)
L = sample length (m)
W = sample width (m)
T = sample thickness (m)

Similarly, the damping signal of the sample is converted to tan δ values by using the equation

$$\tan \delta = CV/f^2$$

where V = DMA damping signal (mV)
C = system constant (0.297 Hz^2/mV)

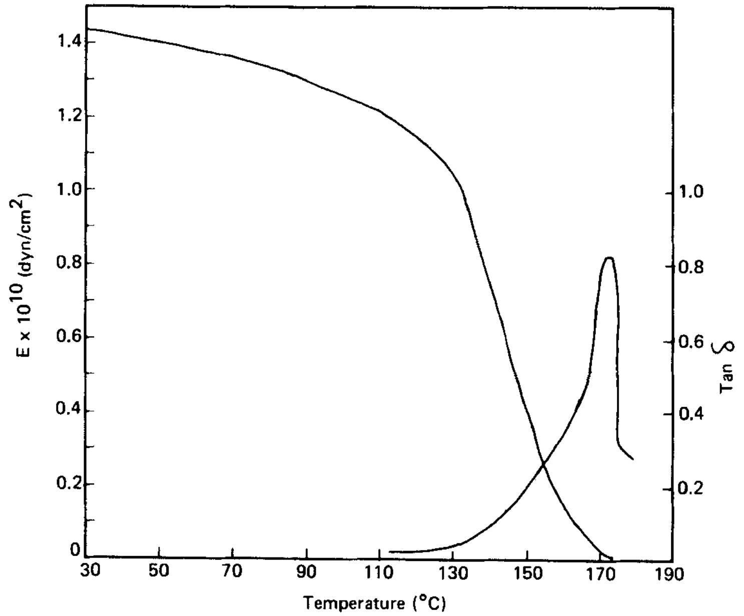

FIG. 5. The dynamic mechanical data of modulus E and tan δ as a function of temperature for PMDNT film.

A plot of Young's modulus E and tan δ against temperature is shown in Fig. 5. As is found for all viscoelastic materials, the modulus decreases with temperature. The modulus decrement is appreciable in the glass transition region. The range of modulus from 1.4×10^{10} to 1×10^8 dyn/cm^2 is covered in the temperature range 40-180°C. The magnitude of the modulus is nearly of the same order as that observed for such other commercial polymers as polystyrene and polymethyl methacrylate.

The damping (tan δ) goes through a maximum as the temperature is raised. It is well known that molecular motions of macromolecules as well as motions of certain segments give rise to dissipation of energy during experiments for mechanical study. This results in the occurrence of maxima in the frequency and temperature dependence of the mechanical loss factor tan δ. For PMDNT, tan δ attains a maximum around 170-175°C. Glass transition temperature and temperature of maximum damping correspond closely to measurements made at low frequencies [17]. Hence T_g is taken as the temperature of maximum damping. This T_g is in good agreement with that obtained by DSC.

The results of viscosity and osmometry are tabulated in Table 2.

TABLE 2. Intrinsic Viscosity [η] in Chloroform at 35°C and Number-Average Molecular Weight of PMDNT Fractions

Fraction	[η] (dL/g)	$\overline{M}_n \times 10^{-4}$
1	0.41	14.0
2	0.31	9.76
3	0.27	7.58
4	0.24	-
5	0.22	5.80
6	0.20	4.74
7	-	4.34

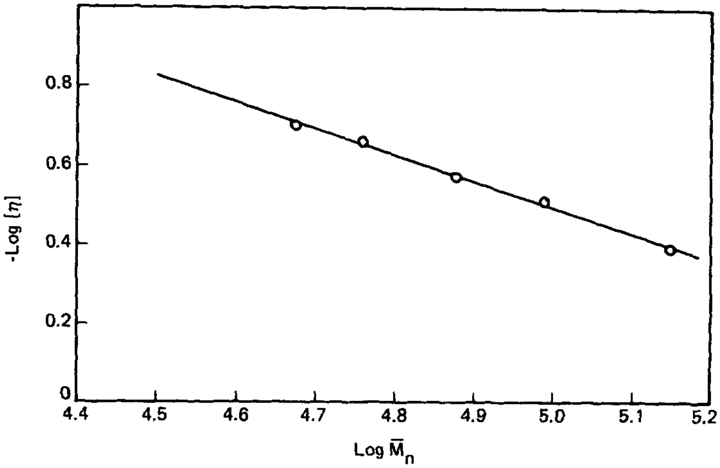

FIG. 6. Dependence of [η] on $\overline{M}_n$ for PMDNT in chloroform at 35°C.

A plot of log [η] versus log $\overline{M}_n$ is shown in Fig. 6. The plot is linear, indicating the applicability of the empirical relationship [η] = KM^{ν}. The line is due to linear regression analysis (correlation > 99%) of the experimental data, and the MHKS relationship derived therefrom is

$$[\eta]\ (\mathrm{dL/g}) = 1.51 \times 10^{-4}\,\overline{M}_n^{\,0.68} \text{ in chloroform at } 35°\mathrm{C}$$

The MHKS exponent ν lies in the range from 0.5 to 0.8, generally observed for polymers that are flexible in solution.

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