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Ultrasonic Velocities and Rao Formulism in Solution of Polyesterimides

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SUMMARY

Ultrasonic velocity measurements have been made in solutions of polyesterimide. It has been observed that by the application of Rao relationship and Nomoto equation, the ultrasonic velocity and density measurement can give useful information about the structural parameters of the copolymers.

INTRODUCTION

The empirically established Rao relationship (RAO 1940, RAO 1941) has been found to be applicable to a large group of liquids (PAPAYUANOV et al. 1973, SETTE et al. 1961, NOZDREW 1965) and solid polymers (SCHUYER 1958; SCHUYER 1959; VAN KREVELEN, HOFTYZER 1976). The Rao constant, R, is given by

$$R = \frac{M}{\rho} v^{1/3} \qquad \ldots (1)$$

where M, ρ , v are molecular weight, density, ultrasonic velocity of the system under study, respectively. R is an additive property and equals to the sum of the group-contribution of various groups present in the molecule (VAN KREVELEN, HOFTYZER 1976; LAGEMANN, CORRY 1944). For binary liquid mixtures the Rao constant, R_m, can be calculated by the Nomoto equation (NOMOTO 1958)

$$R_m = R_1X_1 + R_2X_2 \qquad \ldots (2)$$

where R_1, R_2 and X_1, X_2 are the Rao constants and mole fractions of the liquids 1 and 2 in the mixture. It has been shown that R for polymer solution may be obtained experimentally and theoretically by the use of equations (1) and (2), respectively (REDDY, SINGH 1980a, 1980b, 1980c). In this communication we have tried to test the validity of Rao formulism in copolymer solution such as polyesterimides in DMF.

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EXPERIMENTAL

Materials - All the materials used are either pure grade or purified according to standard procedure before use.

Polymer synthesis

Polyesterimide 1

Polyesterimide 1 was prepared from trimellitic acid anhydride, 4,4'-diamino diphenyl methane and excess ethylene glycol under nitrogen atmosphere. The details of the synthesis was described elsewhere (MAITI, DAS 1978; MAITI, DAS 1980).

Polyesterimide 2

A dicarboxylic acid, N-(O-carboxyphenyl) trimellitimide, was prepared from O-aminobenzoic acid and trimellitic acid anhydride in NN'-dimethyl formamide solution. This dicarboxylic acid was condensed with excess ethylene glycol in presence of zinc-acetate-antimony trioxide as polyesterification catalyst to obtain polyesterimide 2. The details of experimental procedure was described elsewhere (MAITI, DAS 1979).

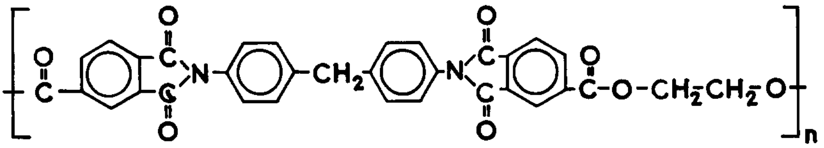
Ultrasonic Measurements

The ultrasonic velocity measurements have been carried out by interferometric technique (HUBBARD 1931) employing Ultrasonic Interferometer, Model M-78 (Mittal Enterprise, New Delhi).

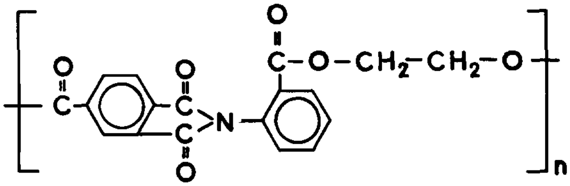
The experimental cell has a double wall jacket and water at 35 ° ± 0.05°C was circulated through it from Thermostat Model U10 (VEB MLW Prüfgeräte-Werk, GDR). The experimental frequency used was 2 MHz and the velocity measurements has got accuracies better than ± 0.5%. The average of at least ten readings are taken for calculating the ultrasonic velocity.

RESULTS AND DISCUSSION

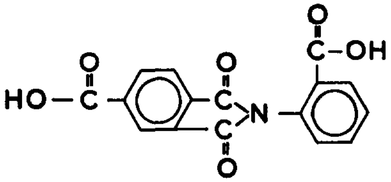
The structure of the repeat units of polyesterimide 1 and polyesterimide 2 as well as the molecular structure of the dicarboxylic acid, i.e., N-(O-carboxyphenyl) trimellitimide are shown below.



(I) Polyesterimide 1



(II) Polyesterimide 2



(III) N-(O-carboxyphenyl) Trimellitimide

The general characteristics of the polymers are shown in Table 1.

TABLE 1

Physical Characteristics of the Polyesterimides

Property	Polyesterimide 1	Polyesterimide 2
Colour	Yellowish brown	Light yellow
T_m^a, °C	250	180
T_g^a, °C	185	100
Inherent viscosity^b	0.17	0.204
Density, g/cm^3	1.24	1.14
Nitrogen, %		
Calcd.	4.89	4.15
Found	4.80	3.95

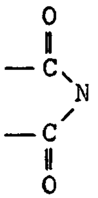
a Calculated from DTA curve (Ref. 6 and 7).
b Inherent viscosity was measured in 0.5% solution in DMF at 30°C.

The ultrasonic velocities vs. concentration of polyesterimides and the dicarboxylic acid in, N,N-dimethyl formamide (DMF) solution at 35°C are shown in Fig. 1. It is observed that the velocity increases with the concentration of the solution. The ultrasonic velocity of the dicarboxylic acid shows higher values than polyesterimide 2.

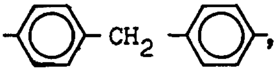
The ultrasonic longitudinal velocity, v, is related to the compressibility, β , and density, ρ , by the following expression

$$v = \left(\frac{1}{\beta\rho} \right)^{1/2} \qquad \ldots (3)$$

The repeat unit of the polyesterimide 1 contains two imide groups,



, joined by the diphenylene methane,



, unit (see structure I).

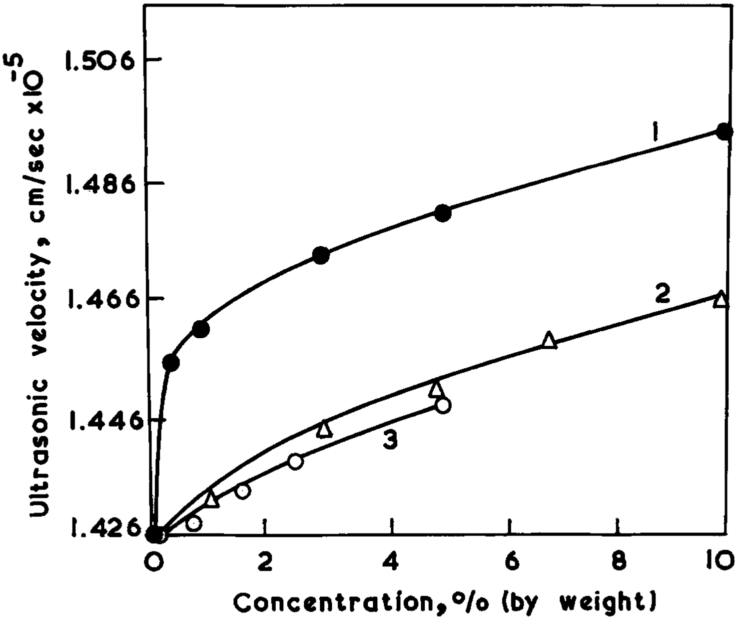


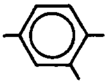
Fig. 1 Ultrasonic velocities in DMF of 1, polyesterimide 1; 2, polyesterimide 2; and 3, N-(O-carboxyphenyl) trimellitimide at 35°C.

This results in a rigid chain. Polyesterimide 2, on the other hand, contains only one imide group (structure II). Moreover, structure I is more symmetric than structure II. It is expected, therefore, that polyesterimide 1 will be more rigid than polyesterimide 2, and consequently the compressibility of the former will be significantly less. The compressibility factor will compensate more for the density term of the equation (3) above. Hence the ultrasonic velocities are higher at all concentrations of the solution of polyesterimide 1 in comparison with polyesterimide 2. The dicarboxylic acid is a small molecular weight organic compound and does not possess the flexibility of a chain molecule such as polyesterimide. This may probably be the reason for higher ultrasonic velocity in this compound than in the polyesterimide 2. However, detailed studies on the chain flexibility and polymer-solvent interaction parameters by ultrasonic techniques are under progress.

Table 2 gives the group contributions of Rao constant for polyesterimide 1 (structure I), polyesterimide 2 (structure II) and N-(O-carboxyphenyl) trimellitimide (structure III), respectively. The Rao constant for the solvent, DMF, calculated from the group contribution is found to be 4,085(cm^3/mole) x (cm/sec)$^{1/3}$.

TABLE 2

Group Contribution for Rao Constant

Group	Rao const.[a] of the group	Contribution to Rao const. for		
		Structure I	Structure II	Structure III
	4,100	8,200	3,450	3,450
	3,700	7,400	3,700	3,700
$-CH_2-$	800	2,640	1,760	-
$-N\langle$	100	200	100	100
$\rangle C=O$	900	3,600	1,800	1,800
$-COO-$	1,250	2,500	2,500	-
$-COOH$	1,430	-	-	2,860
Total		24,540	13,310	11,910

[a] Unit for Rao constant (cm^3/mole) x (cm/sec)$^{1/3}$

The theoretical values of Rao constants for polymer solutions were computed from the Rao constants of solid polymers and the solvent using Nomoto euqation (equation 2).

The experimental values of Rao constants for polymer solutions were determined from ultrasonic velocity and density measurements using equation (1). It is evident from Table 3 that there is a good agreement between the theoretical and experimental values of Rao constants.

TABLE 3

Rao Constant for Monomer and Polymers in Solution at 35°c

Monomer/ Polymers	Conc., %	Rao constant, $(\frac{cm^3}{mole})(\frac{cm}{sec})^{1/3}$		
		Expt.[a]	Theor.[b]	Theor.[c]
Monomer	1	4,086	4,091	4,028
	3	4,120	4,158	4,141
	5	4,160	4,197	4,181
	7	4,195	4,237	4,221
	10	4,261	4,301	4,285
Polyesterimide 1	0.5	4,100	4,115	4,098
	1	4,086	4,128	4,110
	3	4,141	4,182	4,165
	5	4,187	4,238	4,222
	10	4,330	4,387	4,371
Polyesterimide 2	0.5	4,083	4,115	4,098
	1.5	4,093	4,116	4,111
	2.5	4,121	4,154	4,138
	5	4,195	4,205	4,189

[a] Calculated from equation (1).

[b] Calculated from equation (2) with the help of R_1 value determined experimentally.

[c] Calculated from equation (2) with the help of $R_1 = 4{,}085$.

These results indicate the general applicability of earlier findings and offer an additional support for the structure of the repeat units of the polyesterimides 1 and 2, as shown in structures I and II, which have been established by independent methods, such as elemental analysis and IR studies earlier. It is obvious that even the values of the Rao constant in solid state are not available, one can evaluate these values by the measurement of ultrasonic velocity and density in its solution with the help of equations 1 and 2. The Rao constant being an additive property offers an indirect method of testing the structure of the repeat unit of copolymers, particularly copolycondensates. This approach is expected to be useful also for differentiating the structure of repeat unit in isomeric polycondensates.

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