Polymer Bulletin 8, 443–449 (1982)

Polymer Bulletin

Ultrasonic Velocities and Rao Formalism in Solutions of Polyamic Acids of Differing Molecular Structures

R. K. Gupta[1], I.D. Gaba[1], C.D. Pande[1] and R.P. Singh[2]

[1] Defence Science Centre, Metcalfe House, Delhi-110 054, India

[2] Polymer Characterisation Laboratory, Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

SUMMARY

Ultrasonic velocity and density measurements have been made in solutions of polyamic acids of differing molecular structures over extended range of concentration at room temperature. It has been shown that the Rao formalism is applicable to polyamic acid solutions employing Nomoto equation. The consequence of the above finding is discussed for the structural analysis of polymers of complex structures. The flexibility of the polymer chains has also been discussed in terms of the compressibility evaluated from ultrasonic velocity and density data of polymer solution.

INTRODUCTION

The Rao (RAO 1940, RAO 1941) has established a relationship between ultrasonic velocity (v), density (ρ) and molecular weight (M) which has been found to be invariant with temperature and pressure for unassociated organic and inorganic liquids (SETTE 1965; PAPAYUANOV et. al. 1973). The constant 'R' which is

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

known as Rao constant has additive property and is equal to the sum of the group contributions of various groups present in the molecule (VAN KREVLEN, HOFTYZER 1976). Nomoto (NOMOTO 1958) has shown that Rao constant R_m for binary liquid mixtures can be theoretically calculated by the following equation

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

where R_1, R_2 and X_1 and X_2 are the Rao constants and mole fractions of the component liquids in the mixtures. R_m is also experimentally determinable by ultrasonic velocity (v_s) and density measurement (ρ_s) in liquid mixtures.

$$R_m = \frac{M_s v_s^{1/3}}{\rho_s} \qquad \ldots (3)$$

where $M_s = X_1M_1 + X_2M_2$; M_1 and M_2 being the molecular weights of

0170-0839/82/0008/0443/$ 01.40

component liquids.

It has been observed that Rao constant of solid polymers can be also evaluated by an equation (SCHUYER 1958 and 1959)

$$R = \frac{M}{\rho} v^{1/3} \left[\frac{1+\nu}{3(1-\nu)} \right]^{1/6} \qquad \ldots (4)$$

where ν is the Poisson's ratio. For most of the polymers $\nu \approx 0.5$, hence the value of the additional multiplying factor is nearly equal to 1. Consequently equation (4) reduces to equation (1) for most of the polymers. It has been recently shown (REDDY et.al. 1981; BAGCHI, SINGH 1982) that the theoretical values obtainable from the addition of group contributions are equal to the experimental values evaluated from equation (1).

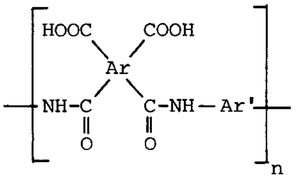
Mainly due to the bonding problems of piezoelectric crystal on solid polymers, the ultrasonic velocity measurements in solid polymer are tedious. However, the ultrasonic velocity measurements in polymer solutions are much simpler, faster and more accurate. Recently it has been observed that the Nomoto equation (2) is also applicable in the solutions of polymers of differing molecular structure (SINGH et.al. 1980; REDDY, SINGH 1980a, 1980b; REDDY et.al.1981; BANDOPADHYAY et.al. 1981). Das et.al.(1980) have applied this formalism in the solutions of some polyesterimides. The present paper discusses the validity of Rao formalism in solutions of a series of polyamic acids of quite complex nature. The paper also describes the molecular interpretation of compressibility of polymer solutions.

EXPERIMENTAL

Materials

A series of polyamic acids were synthesised from various purified dianhydrides and diamines, in purified N, N-dimethylacetamide (DMAc) solvent. The details of the synthesis would be given elsewhere (GUPTA 1982). The solutions of polyamic acids in DMAc at various concentrations were studied.

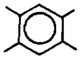
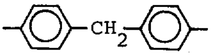
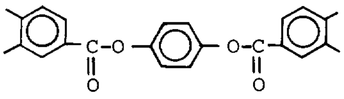
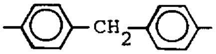
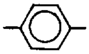
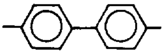
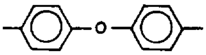
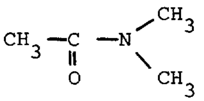
The general structure of the polyamic acids is represented by the formula,



where Ar and Ar' are various structural residues from dianhydrides and diamines as described in Table I.

TABLE I

Structural Formulae of Polyamic Acids and Solvent

Polyamic Acid	Dianhydride Residue Ar	Diamine Residue Ar'
I	 (PMDA)	 (DDM)
II	 (PPBTA)	 (DDM)
III	(PPBTA)	 (PPDA)
IV	(PPBTA)	 (Benzidine)
V	(PPBTA)	 (DDPE)
Solvent	 $CH_3-C(=O)-N(CH_3)_2$ (DMAc)	

Ultrasonic and Density Measurements

The ultrasonic measurements have been carried out by ultrasonic interferometric technique. Constant temperature was maintained by thermostat model U10 (VEB MLW, Prufgerate-Werk, GDR). The accuracy in ultrasonic velocity and temperature stability is better than ± 0.5% and ± 0.1°C respectively. The details of measurements have been described earlier (REDDY, SINGH 1980). The densities of solvent and solutions have been obtained from specific gravity bottle.

RESULTS AND DISCUSSIONS

The ultrasonic velocities increase with concentration in all the studied polyamic acids. The addition of polymer makes a positive change in the ultrasonic velocity of polymer solution in conformity with the literature (SETTE 1961).

The theoretical values of the Rao constants evaluated by the addition of group contributions (VAN KREVELEN, HOFTYZER 1976) for solvent and different polyamic acids have been compiled in the Table II. In case of solvent, dimethylacetamide, the experimental value of Rao constant has been evaluated from molecular weight = 87.078, density = 0.932 gm/cc and experimental ultrasonic velocity = 146080 cm/sec at 23°C. The theoretical (5015) and experimental values (4920) are differing only by 1.9% which is well within experimental error.

TABLE II

The Theoretical Values of Rao Constant and Molecular Weight of Different Polyamic Acids and Solvent

Sl. No.	Polyamic acid or solvent		Theoretical value of Rao constant from addition of group contributions ($cm^{10/3}$ $sec^{-1/3}$ mol^{-1})	Molecular Weight
1.	Dimethyl Acetamide		5015	87.078
2.	Polyamic Acid	I	18830	416.136
3.	"	II	29480	656.196
4.	"	III	24500	366.148
5.	"	IV	28600	642.148
6.	"	V	29000	658.183

The theoretical values of Rao constant using Nomoto equation (2) and the experimental values of Rao constant calculated from equation (3) have been given in Table III for all polymer solutions, studied under present investigation. It may be observed that the theoretical and experimental values are very close in all polymer solutions at various concentrations. The present investigation gives credence to the earlier findings of the authors in number of other systems (SINGH et. al. 1980, REDDY, SINGH 1980a, 1980b REDDY et.al. 1981, BANDOPADHYAY et.al. 1981) and seems to be generalised feature of all polymer solutions

TABLE III

The Experimental Values of Compressibility and Experimental & Theoretical Values of Rao Constants at Various Concentrations in Polyamic Acid Solutions

Polyamic acid	% concentration	Compressibility (β) x 10^{11} cm sec^2/g	Rao constant $cm^{10/3} sec^{-1/3} mol^{-1}$ Experimental	Theoretical
I	9.14	4.648	5137.8	5206.03
	5	4.800	5033.6	5077.60
	2	4.900	4963.0	4985.06
	1	4.995	4948.8	4942.69
	0.5	5.044	4938.0	4935.72
II	4	4.8520	5038.0	5062.45
	2	4.9260	4975.0	4990.34
	1	5.0090	4962.0	4955.56
	0.5	5.0190	4944.7	4937.78
III	3	4.9636	5004.4	5017.90
IV	7.2	4.6510	5133.9	5165.42
	2	4.9480	4980.3	4989.82
	0.5	5.0230	4938.4	4937.29
V	4	4.8600	5028.0	5060.24

By rearranging Nomoto equation,

$$R_1 X_1 = R_2 X_2 - R_m \qquad \ldots (5)$$

the Rao constant for solid polymers may be obtained from the experimental values of Rao constants of the solution and solvent

The Rao constant of solid polymer, being an additive quantity where each functional group makes an independent contribution, may be used in structural analysis.

The compressibility (β) of a polymer solution can be obtained from ultrasonic velocity and density data by following equation.

$$\beta = \frac{1}{\rho v^2} \qquad \ldots (6)$$

The compressibility data has been tabulated in Table III. The polymer makes an additive contribution to the compressibility of solvent (NOZDREV 1965). In the present case, the solvent is same in all cases. Hence the polymer solution compressibility would reflect the contribution of polymer itself, which is also supported by the following discussion.

It is obvious from the structures of the various polyamic acids that I and IV contain parabenzene groups along with the imide group in the main chain. The former does not have ester group. The compressibilities of their solutions also show very low values accordingly due to lack of consequent flexibility of polymer chains. Structurally II and V have almost same flexibility. At the same concentrations, their compressibilities in solutions are of same values within the experimental error.

The solvation number of some of the polyamic acids have been calculated by using Passynsky relation (PASSYNSKY 1948, MAJUMDAR et. al. 1980).

$$n = \left(1- \frac{\beta}{\beta_o} \right) \left(\frac{100-x}{x} \right) \qquad \ldots (7)$$

where β is the adiabatic compressibility of the solution, β_o that of the solvent and x is the number of grams of polymers in 100 gm of the solution. The number of solvated molecules per polymer repeat unit, S may be obtained from equation (7) by multiplying "n" with the molecular weight of the polymer repeat unit. The solvation number at zero concentration S_0 is obtained by extrapolating the S versus concentration curve at zero concentration. Their values for polyamic acid I, II and IV solutions in DMAc come out to be equal to 5 which is the indicator of the uniform polymer solvent interaction in all these polymer solutions, hence the above discussed compressibility behaviour is the reflection of the rigidity of the polymer chains only.

ACKNOWLEDGEMENT

Authors thank Dr. A.K. Banthia for helpful discussion.

REFERENCES

1. BAGCHI S. and SINGH R.P., Acustica (1982) (In press)
2. BANDOPADHYAY P.C., MAITI A.K., CHAKI T.K. and SINGH R.P., Acustica, 50, 75 (1982)
3. DAS S., SINGH R.P. and MAITI S., Polymer Bulletin 2, 403 (1980)
4. GUPTA R.K. (Patent being applied)
5. MAJUMDAR S., HOLAY S.H. and SINGH R.P., Euro. Polym.J. 16,1201 (1980)
6. NOMOTO O.J., Phys. Soc. Japan 13,1528 (1958)
7. NOZDREV, V.F., THE USE OF ULTRASONICS IN MOLECULAR PHYSICS, Pergamon Press Book Distributed by the McMillan Company, New York, N.Y.(1965) pp 82-155
8. PAPAYUANOV A., HART T.R. and ANDREWS R.D., J. Chem. Phys. 53, 109 (1973)
9. PASSYNSKY A., Acta Phys/Chem. USSR 22, 317 (1943)
10. RAO, M.R., Ind. J. Phys. 14, 109 (1940)
11. RAO, M.R., J. Chem. Phys. 9, 682 (1941)
12. REDDY G.V. and SINGH R.P., Acustica 46, 229(1980)
13. REDDY G.V. and SINGH R.P., Acustica 46, 342(1980)
14. REDDY G.V. MAJUMDAR S. and SINGH R.P., Acustica 47, 343(1981)
15. REDDY G.V., CHATTOPADHYAY S., SINGH Y.P. and SINGH R.P., Acustica, 48,347 (1981)
16. SCHUYER J., Nature 181, 1394 (1958)
17. SCHUYER J., J. Polym. Sc. 36, 475 (1959)
18. SETTE D., HANDBUCH DER PHYSIK, Vol.LXI/1,S.F. LÜGG (Ed.) SPRINGER VERLAG, BERLIN (1961) pp 339-354
19. SINGH R.P., REDDY G.V., MAJUMDAR S., SINGH Y.P., Rheology 2, 309 (1982)
20. VAN KREVELEN D.W. and HOFTYZER P.J., PROPERTIES OF POLYMERS, Elsevier Scientific Publishing Company,Amsterdam, Chap.3, 1976

Received April 16, accepted after revision August 23, retyped September 27,82

C