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INVESTIGATIONS ON AROMATIC POLYESTERS WITH POLYNAPHTHALENE SYSTEMS IN THE MAIN CHAIN—X

STUDIES ON THE DETERMINATION OF CHEMICAL INHOMOGENEITY OF AROMATIC COPOLYESTER CHAINS

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Abstract—The turbidimetric titration technique was applied to determine, for a number of solvent-non-solvent systems, the relation between the parameter γ^* and the content of 2,2 bis(4-hydroxyphenyl) propane in the terephthalic copolyester of 4,4′ dihydroxydinaphthyl 1,1′ and 2,2 bis(4-hydroxyphenyl) propane. A system most sensitive to differences in the chemical composition of the copolyester was found and then used to fractionate two copolyesters obtained in different reaction conditions and having the same composition but differing in the arrangement of comonomer units in the chain. Fractionation results have been presented in the form of MWD curves and also as a relation between the content of 2,2 bis(4-hydroxyphenyl) propane and the intrinsic viscosity $[\eta]$ of individual fractions.

INTRODUCTION

Synthetic homopolymers and copolymers obtained in polymerization and polycondensation reactions are inhomogeneous as regards chain length i.e. they have a definite molecular weight distribution. In the case of copolymers however, except for the strictly alternating copolymers, molecular size inhomogeneity may be accompanied by chemical composition inhomogeneity of individual polymer chains. Depending on the reactivities of comonomers and reaction conditions, the sequence in which individual units are built into the growing polymer chain may be random (a random copolymer) or there may be longer sequences of one of the units (a block copolymer). Determination of the content of one of the comonomers in individual copolymer fractions makes it possible to gain an insight into the compositional heterogeneity of copolymers.

The copolymer fractionation process, taking into account compositional variations, has been described by the following equation by Topchiev [1]

$$V'_{r,\alpha}/V_{r,\alpha} = \exp[r(\sigma + K\alpha)] \qquad (1)$$

where $V'_{r,\alpha}$ and $V_{r,\alpha}$ are the respective volume fractions of the component having a degree of polymerization r and a chemical composition α (volume fraction or molar fraction of the monomer A in the copolymer A–B) in the precipitate and dilute solution phases. σ is a fractionation parameter (partition coefficient).

It follows from the above equation that the efficiency of fractionation with respect to chemical composition depends on the magnitude of the parameter K. For a ternary system (solvent–precipitant–copolymer), the following expression for the parameter K has been given by Teramachi [2].

$$K = (v_1 - v'_1)(\chi_{1A} - \chi_{1B}) + (v_2 - v'_2)(\chi_{2A} - \chi_{2B}) \qquad (2)$$

where: v_1 and v_2 are the volume fractions of solvent and precipitant, respectively χ_{1A}, χ_{1B} and χ_{2A}, χ_{2B} are respectively the coefficients of interaction between the solvent and the precipitant with the monomers A and B.

The solvent–precipitant system in which the differences between the coefficients of interaction of the solvent and the precipitant with individual monomers will be the largest, may thus be regarded as being the best system for fractionating the copolymer with respect to chemical composition.

Cloud-point titration was found to be the preferred method when trying to select the optimum solvent-non-solvent system by Stockmayer and co-workers, who were the first to use it for the fractionation of a copolymer of styrene and methyl methacrylate [3]. Litmanovich *et al.* [4] proposed, for the selection of a suitable solvent-non-solvent system, the use of values of the parameter γ^* (volume fraction of non-solvent required for the onset of precipitation) determined for a number of copolymers having a wide range of chemical heterogeneity.

In a system in which the values of the parameter γ^* are strongly dependent on chemical composition, the fractionation of a copolymer will mainly reflect the difference in the chemical structure of macromolecules. The problem of selecting an optimum system for cloud point titration was also studied by Elias *et al.* [5–6]. It was the aim of the present work to study the relation between the structure of macromolecules and their chain length, and to determine the influence of polymer synthesis conditions on the chemical heterogeneity of terephthalic copolyesters of 4,4′ dihydroxydinaphthyl 1.1′ and 2,2 bis(4-hydroxyphenyl) propane, obtained for the 50:50 mol ratio of bisphenolic components.

Earlier investigations had indicated the reaction conditions to influence the overall content of alternating structures in the polymer chain.

Based on cloud point determinations for a number

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Table 1. Structure of the terephthalic (T) copolyester chains of 4,4′ dihydroxydinaphthyl 1,1′ (N) and 2,2 bis(4-hydroxyphenyl) propane (D), determined by NMR [8, 10]

Sample	Percentage structure content NTN	NTD	DTD	Degree of randomness
Random copolymer	24.5	51.4	24.1	1.03
Block copolymer	29.6	40.2	30.2	0.80

of solvent-non-solvent systems, it was possible to find an optimum system for the fractionation of the terephthalic copolyesters of 4,4′ dihydroxydinaphthyl 1,1′ and 2,2 bis(4-hydroxyphenyl) propane with respect to chemical composition. Two samples of copolyesters synthesized by different methods were fractionated, and their molecular weight and compositional distributions determined.

EXPERIMENTAL

Materials

Terephthalic copolyesters of 4,4′ dihydroxydinaphthyl 1,1′ (N) and 2,2 bis(4-hydroxyphenyl propane) (D), prepared by a low-temperature solution method, were used [7]. Since the terephthalic homopolyesters of these bisphenols are practically insoluble in the solvents used for the fractionation, the cloud-point determinations were performed for copolyesters having a different mol ratio of the bisphenolic comonomers, varying in the range from N:D = 10:90% mol to N:D = 90:10% mol (designated by symbols N10–N90).

Fractionation was carried out for two copolyester samples in which the molar ratio of bisphenolic components N:D was 50:50. One of the copolyesters was synthesized in conditions leading to the formation of a random copolymer (triethylamine acting as a catalyst is added to a methylene chloride solution of comonomers: 4,4′ dihydroxydinaphthyl 1,1′ and 2,2 bis(4-hydroxyphenyl) propane and the intermonomer–terephthaloyl chloride); the other was made in reaction conditions favouring the formation of a block copolymer (the solution of the intermonomer–terephthaloyl chloride in methylene chloride was added at a rate of 10 ml/min to the solution of the comonomers and triethylamine in methylene chloride). The terms random copolymer and block copolymer are to be understood as those postulated by Yamadera and Murano [8] on the basis of the degree of randomness, taking into account the content of homolinkages and heterolinkages in the polymer chain. The two studied copolyesters differed both as regards the content of homo units (NTN, DTD) and hereto units (NTD) in the polymer chains. The chain structure was determined by an NMR technique [10] with results listed in Table 1. The content of one of the bisphenolic components in individual fractions, viz. 2,2 bis(4-hydroxyphenyl) propane, was determined by i.r. analysis [11].

The relative absorption i.r. studies for the analytical band of 1506 cm^{-1} and the reference band of 876 cm^{-1} for mixtures containing different amounts of the copolyester and the poly[2,2 bis(4-hydroxyphenyl) propane terephthalate] (homopolymer) made it possible to derive the following equation for quantitative determination of 2,2 bis(4-hydroxyphenyl) propane in the copolyester fractions:

$$c_1 = 0.555\ \mathrm{B} - 0.509$$

where,

c_1 = the content of 2,2 bis(4-hydroxyphenyl) propane
B = A^{1506}/A^{876}-relative absorption in the 1506 cm^{-1} and 876 cm^{-1} bands

The i.r. spectroscopic technique yielding the total of 2,2 bis(4-hydroxyphenyl) propane was found in our case to be more useful and accurate than the NMR investigations which gave the content of the NTN and DTD homo units and the NTD hetero units separately.

Cloud-point titration

In order to determine a suitable solvent-non-solvent system, 0.02% solutions of the investigated terephthalic copolyesters were prepared in chloroform, tetrachloroethane and methylene chloride. These had contents of the 4,4′-dihydroxydinaphthyl 1,1′ ranging from N10 to N90. Acetone, methanol and ethanol were used as precipitants. The turbidimetric titrations were carried out using a SPEKOL (Carl Zeiss Jena) spectral colorimeter. The polymer solution investigated was introduced into the measuring cell and then a micro-dose pump was used to deliver the non-solvent into the cell, the contents of which were agitated at constant rate during the experiment. The experimental cloud point curves were thus recorded. Sol-

Table 2. Volume fractions of the precipitant [100 × (V_p/V_s)] at the cloud point

Solvent	Non-solvent	Copolyesters* N10	N20	N30	N40	N50	N60	N70	N80	N90
Chloroform	Acetone	—	43.3	34.0	29.3	26.0	21.3	18.7	14.7	—
	Methanol	—	34.7	28.7	26.7	24.7	22.0	19.3	16.3	—
	Ethanol	—	44.0	35.5	32.7	29.3	26.0	22.7	20.7	—
Methylene chloride	Acetone	—	43.0	34.0	28.0	22.7	16.0	12.0	—	—
	Methanol	—	26.7	23.0	20.0	19.3	16.7	14.0	—	—
Tetrachloroethane	Acetone	100	82.0	74.0	63.3	60.7	49.3	48.0	37.3	23.3
	Methanol	50.7	43.3	39.3	38.0	37.3	35.3	32.7	29.3	28.0
	Ethanol	65.0	55.3	48.7	49.3	47.3	48.0	42.0	37.3	34.7

* The symbol N10 corresponds to the copolyester containing 10 mol% 4,4′ dihydroxydinaphthyl 1,1′ (N) and 90 mol% of 2,2 bis(4-hydroxyphenyl) propane (D). Similarly, the symbol N90 corresponds to the copolyester containing 90 mol% of N and 10 mol% of D.

Table 3. Results for the fractions of the random copolyester

Fraction symbol	w_i	Bisphenol A* content % mol	$[\eta]_{25}$ [dl/g] $CHCl_3$
I	0.1510	46.7	1.22
II	0.1142	46.9	0.88
III	0.1003	43.1	0.70
IV	0.0688	47.8	0.64
V	0.0838	47.1	0.58
VI	0.0853	45.9	—
VII	0.0489	46.5	0.43
VIII	0.0954	46.4	0.36

* Bisphenol A is a common name for 2,2 bis(4-hydroxyphenyl) propane.

vents and precipitants were purified using standard techniques [12].

Fractionation

The fractionation was performed at 25° in a thermostated column, 1% solutions of the copolyesters being used. Individual fractions were obtained by adding dropwise acetone into the column until the first haze (onset of precipitation) appeared. The column was then heated up to the temperature at which the fractionation mixture again became clear (the first fractions were insoluble on heating up the system) and allowed to cool slowly to the fractionation temperature. The phase separation process was found to last 2–3 days. The precipitate was dissolved in excess tetrachloroethane and added dropwise into an excess of acetone to re-precipitate the fraction. The fractions were dried in a vacuum oven at 70°.

DISCUSSION OF RESULTS

Cloud-points obtained by the turbidimetric titration of solutions of terephthalic copolyesters with different contents of 4,4′-dihydroxydinaphthyl-1,1′ (N) are listed in Table 2.

The amount of non-solvent required to bring about the onset of precipitation (first haze) was found, for all systems studied, to decrease with increase of the content of the bisnaphthol (N). This effect is thought to be due to the size of the molecules of 4,4′-dihydroxydinaphthyl-1,1′ which are larger and more rigid than those of 2,2 bis (4-hydroxyphenyl) propane, and hence their solubility is lower. The said decrease of the amount of the solvent required for the onset of precipitation was found to be largest for acetone as precipitant in the cloud-point titrations of the copolyester solutions in tetrachloroethane. In the light of investigations of Litmanovich *et al.* [4], the latter system should be thus regarded as being the most sensitive to the differences in the molecular structure of macromolecules. Consequently, it was decided to fractionate copolyesters with the 50:50 mol ratio of bisphenolic compounds, and having different polymer chain structures as determined by NMR analysis, in the system tetrachloroethane (solvent)–acetone (non-solvent). The random copolyester was split into eight fractions, and the block copolyester into nine. The i.r. technique was used to determine the contents of 2,2 bis(4-hydroxyphenyl) propane.

Table 4. Results for the fractions of the block copolyester

Fraction symbol	w_i	Bisphenol A content % mol	$[\eta]_{25}$ [dl/g] $CHCl_3$
I	0.2397	31.8	2.57
II	0.1210	33.4	1.40
III	0.1380	32.4	1.37
IV	0.1150	34.2	1.31
V	0.1331	39.8	0.70
VI	0.0955	43.3	0.63
VII	0.0886	44.9	0.59
VIII	0.0586	48.6	0.47
IX	0.0102	46.7	0.29

The Fica automatic viscometer was then used to determine the intrinsic viscosities for the individual fraction at 25° in tetrachloroethane. Results are given in Tables 3 and 4.

The fractionation data for the two copolyester samples were then used to derive their molecular

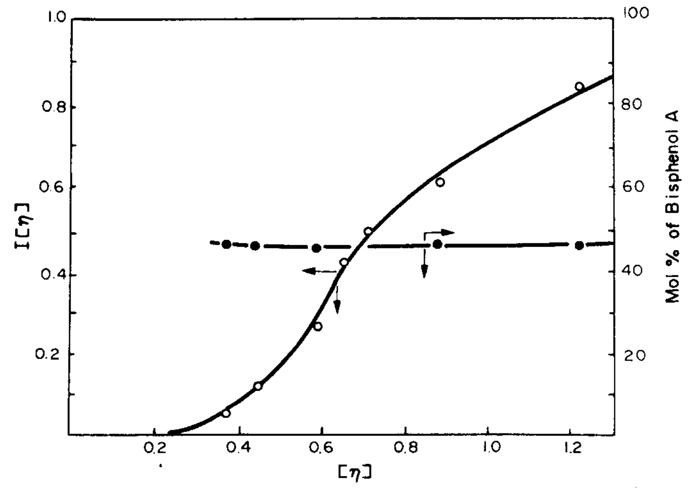

Fig. 1. Random copolyester MWD and content of 2,2 bis(4-hydroxyphenyl) propane (Bisphenol A).

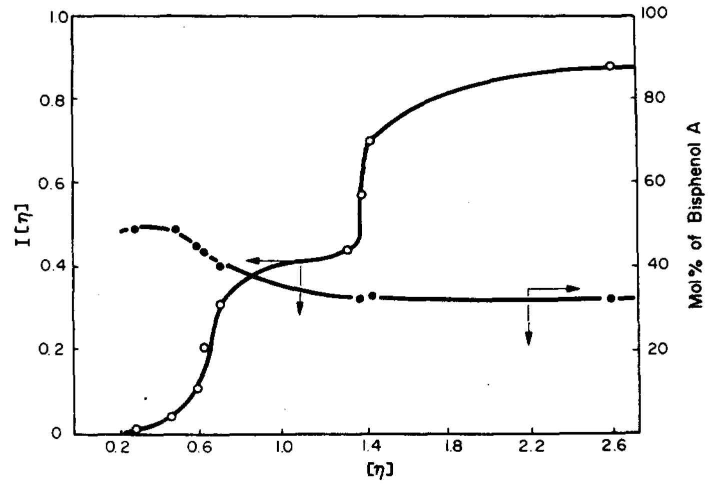

Fig. 2. Block copolyester MWD and content of 2,2 bis(4-hydroxyphenyl) propane.

weight distribution curves, expressed as a function of their intrinsic viscosity [7] by a method due to Schulz [13]. The experimental data were also used to obtain a curve depicting the content of 2,2 bis(4-hydroxyphenyl) propane as a function of [η] for the individual fractions of the copolyesters.

Figure 1 shows fractionation results for the random copolyester. Fractions of that copolyester may be seen not to differ within experimental error as regards chemical composition, the average content of 2,2 bis (4-hydroxyphenyl) propane being 46.3%. Consequently, chains of various length were found to have almost the same chemical composition.

Figure 2 shows fractionation results for the block copolyester. In this case the integral molecular weight distribution curve is bimodal, the content of 2,2 bis(4-hydroxyphenyl) propane changing in individual fractions from 32% for higher molecular weights up to 48% for low molecular weights. The bimodal character of the molecular weight distribution curve was not however confirmed by GPC analysis, where a single peak was obtained.

Owing to the fact that the molecular weight distribution curve was derived with respect to the intrinsic viscosity [η], known to be influenced by both molecular weight and chemical composition of the polymer, the abrupt increase of viscosity between fractions IV and V may be explained in terms of a significant difference in the chemical compositions of individual polymer chains.

This view is well supported by results of the analysis of the chemical composition of individual fractions; the content of 2,2 bis(4-hydroxyphenyl) propane decreases with increasing polymer chain length.

CONCLUSIONS

1. Among the various solvent/non-solvent systems studied, the tetrachloroethane-acetone was found to be most sensitive to differences in the chemical composition of the terephthalic copolyesters of 4,4′ dihydroxydinaphthyl 1,1′ and 2,2 bis(4-hydroxyphenyl) propane.

2. For the copolyester synthesized under conditions favouring formation of a random copolymer, the chemical composition of its macromolecules was found to be independent of molecular weight.

3. For the block copolyester, the content of 2,2 bis (4-hydroxyphenyl) propane was found to decrease and that of 4,4′ dihydroxydinaphthyl 1,1′ to increase with increasing molecular weight.

Summing up, it may be stated that the actual polycondensation reaction conditions influence not only the total content of alternating structures but also the chemical composition of the macromolecules of the two investigated terephthalic copolyesters of 4,4′ dihydroxydinaphthyl 1,1′ and 2,2 bis(4-hydroxyphenyl) propane.

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REFERENCES

1. A. V. Topchiev, A. D. Litmanovich and V. Ya. Shtern, *Dokl. Akad. Nauk SSSR* **147**, 1389 (1962).
2. S. Teramachi and M. Nagasawa, *J. Macromolek. Sci.-Chem.* **A2**, 1169 (1968).
3. W. H. Stockmayer, L. D. Moor Jr, M. Fixman and B. N. Epstein, *J. Polym. Sci.* **16**, 517 (1955).
4. A. D. Litmanovich, V. Ya. Shtern and A. V. Topchiev, *Neftekhimiya* **3**, 217 (1963).
5. H. G. Elias, *Makromolek. Chem.* **33**, 140 (1959).
6. H. G. Elias and U. Gruber, *Makromolek. Chem.* **78**, 72 (1964).
7. Z. Jedliński and D. SęK, *Eur. Polym. J.* **7**, 827 (1971).
8. R. Yamadera and M. Murano, *J. Polym. Sci. A1* **5**, 2259 (1967).
9. D. Sęk, *Eur. Polym. J.* **13**, 967 (1977).
10. Z. Jedliński, D. Sęk and B. Dziewięcka, *Eur. Polym. J.* **13**, 871 (1977).
11. Unpublished results.
12. J. A. Riddick and W. B. Bunger, *Organic Solvents*. Wiley-Interscience, New York (1970).
13. G. V. Schulz, *Z. phys. Chem.* **B46**, 137 (1940); **B47**, 155 (1940).