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CONTRIBUTION TO THE DETERMINATION OF CHEMICAL COMPOSITION OF COPOLYMERS BY MEANS OF GEL PERMEATION CHROMATOGRAPHY

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Abstract. The determination of chemical composition by means of GPC is discussed on the basis of statistical and block co-polymers from styrene-butadiene or α-methylstyrene-butadiene. This method can be used when the refractive index increment (dn/dc) of the copolymers is the sum of the refractive index increments of homo-polymers. In addition, the dependence of extinction coefficent from the sequence length, and the dependence of the refractive index of the polymer from molecular weight, were considered. The GPC results were in good agreement with those obtained from IR and NMR spectroscopy.

Recently, the Gel Permeation Chromatograpy (GPC) has become a fast and reproducible method for the determination of molcular weight distribution.[1,7],a.b.c. The gels that are used have a structure which is bulky for the chromatographic process. Because the GPC method is based on delayed diffusion of the polymer molecule in the pores, one can only expect a separation according to the molecular size, since for smaller molecules the pores are more accessible than for the larger ones. This separation according to the molecular size is not only expected for the homopolymers, but also for the copolymers.

In this work the investigation was made inorder to apply the GPC method for determining chemical composition of block and statistical copolymers. For such investigations one requires a detector combination that can make a simultaneously continuous determination of the total amounts of the copolymer and the partial concentration of a component possible. For example, styrene in copolymer with butadiene can be determined with the help of UV instrument at 254 nm.

When refractometric and the spectrophotometric curves show the same shape, then the copolymer under investigation is considered as chemically homogeneous in respect to the chemical composition within the GPC separation. If both curves have different shapes then chemical heterogenity is demonstrated.

This problem was investigated on statistical and block copolymers from styrene-butadiene and α-methylstyrene-butadiene which were produced from different polymerisation techniques.

The GPC results were compared with those obtained from NMR and IR spectroscopy.

Experimental

We used LKB–UV-instrument which in our case record the α-methylstyrene component at wavelength λ = 254 nm. This instrument is also often used for concentration measurements of protiens solutions and other biochemical substances. It can only be used for such solutions which have no specific absorption in the UV range. We used Waters-filling device[8] to fill our separation column. We have not presented a schematic representation of the GPC chromatographs because it has already been described in detail[9].

Polystyrene, poly α-methylstyrene and polybutadiene which were produced by anionic polymerisation, were used as standard substances. The molecular weight range varied from (i) Polystyrene from 900-1, 800,000; (ii) Poly α-methylstyrene from 2000 - 4000,000; (iii) Polybutadiene from 1000 - 400,000; The polydisparity ($d = \overline{M}_w/\overline{M}_n$) was 1.2-1.06 for the polystyrene For poly α-methylstyrene and polybutadiene this value between 1.02 and 1.05, was calculated. A detailed description of these polymers has already been given[10].

Statistical and block copolymers were studied. The α-methylstyrene butadiene copolymers were produced by anionic polymerisation with Li-Butyl catalyst at -75° and the styrene butadiene copolymers by radical polymerisation at +50° with Redox catalyst. The GPC analysis was done in tetrahydrofuran (THF) at 40°. We used styrenedivinyl-benzene gel with various permeabilities as the stationary phase. The recording of the GPC curves was done with the aid of a differential refractometer and a UV instrument which were continuously switched on. All the butadiene and copolymer samples were initially filtered to prevent an eventual blocking of the separating column.

Results and Discussion

Initially we investigated the homopolymers from polybutadiene, polystyrene and poly α-methylstyrene. The GPC curves are shown in Fig. 1. From Fig. 1 it can be shown that polybutadiene showed no UV absorption at a wave length λ = 254 nm. This value was recorded for polystyrene and poly α-methylstyrene within the limits of GPC accuracy.

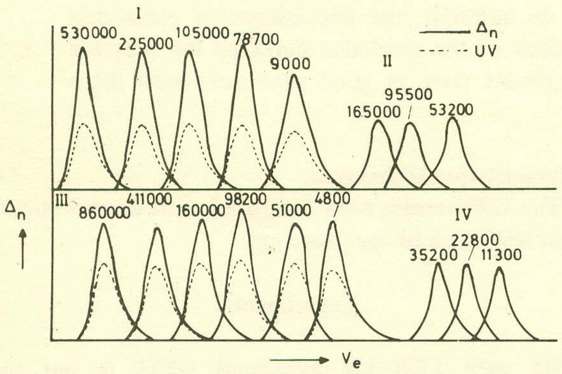

Fig. 1. GPC curves of polystyrene, polybutadiene and poly α-methylstyrene in THF., Column combination $10^5 + 10^4 + 10^3 + 10^2 + 60$ Å; Temperature: 40° 1 = Poly α-methylstyrene (M_n)Os; II, IV = Polybutadiene (M_n) Os; III = Polystyrene (M_w)Ls.

With GPC, the separation of the dissolved macromolecules take place according to their molecular dimensions in solution, because the molecular volume in the first case only depends on the degree of polymerisation, the separation in general proceeds according to different molecular sizes. Certainly by chemically non-homogeneous copolymers which are built from monomers of different polarities, the influence of chemical disorder is quite noticeable because the molecular volume also depends upon the degree of solvation. Moreover, absorption accuracy still appears.

The Waters equipment as already said was provided with a differential refractometer and an additional UV apparatus.

It is thus possible to determine the composition of the copolymers because the differential refractometer registers both components together and the UV apparatus on the otherhand (at approximate wave length) registers only one component. At λ = 254 nm the absorption coefficient of polybutadiene, in contrast with that of polystyrene and poly α-methylstyrene is negligible. While the refractive index difference between solution and solvent at the exit of the column is proportional to the polymer concentration. The transmission (Dx) in the UV range depends on the logarithm of the polymer concentration in accordance to the Lambert-Beer Law.

$$\text{Log}\,\frac{J}{J_o} = \text{Log}\,D_x = -E = -\,\Sigma_k\,.C.\,S. - (1)$$

For the calculation of styrene butadiene and α-methylstyrene-butadiene portion in the copolymer, we needed a direct calibration of the refractometer and the UV instrument. In addition, the homopolymers (polystyrene, polybutadiene and poly α-methylstyrene) in a dilute state were calibrated. These calibration curves are shown in Fig. 3 A & B.

The calculation of the styrene-butadiene and α-methylstyrene-butadiene portions in the complymer from the GPC curves resulted according to the already shown example, (Fig. 2).

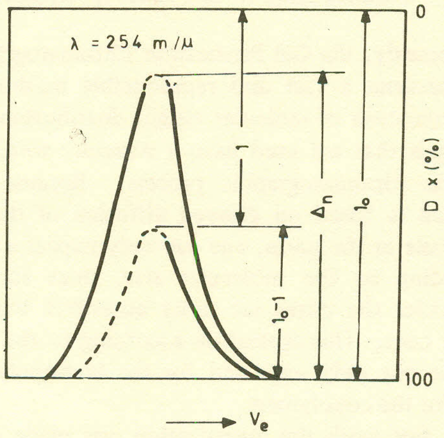

Fig. 2. Shows the GPC curves obtained from the refractometer and UV instrument.

The chromatogram was divided into equivalent strips and for each V_{ei} value, the corresponding transmission (Dx) from the experimental GPC chromatogram was obtained and converted to the extinction (E) see equation 1. Afterwards from V_{ei} value the extinction was arranged with the help of the calibration E=f (c) and in this way, the experimental UV curve was converted into an extinction curve. The remaining curve then yielded the butadiene portion in the copolymer.

This simple way of calculation of gross chemical composition of copolymers with the help of GPC method is only then possible if the refraction increments (dn/dc) of the copolymers additively compose of the homopolymer, that is when $(dn/dc)_{SB} = c_S(dn/dc)_S + c_B(dn/dc)_B$ (2) is valid. c_S and c_B are the mass

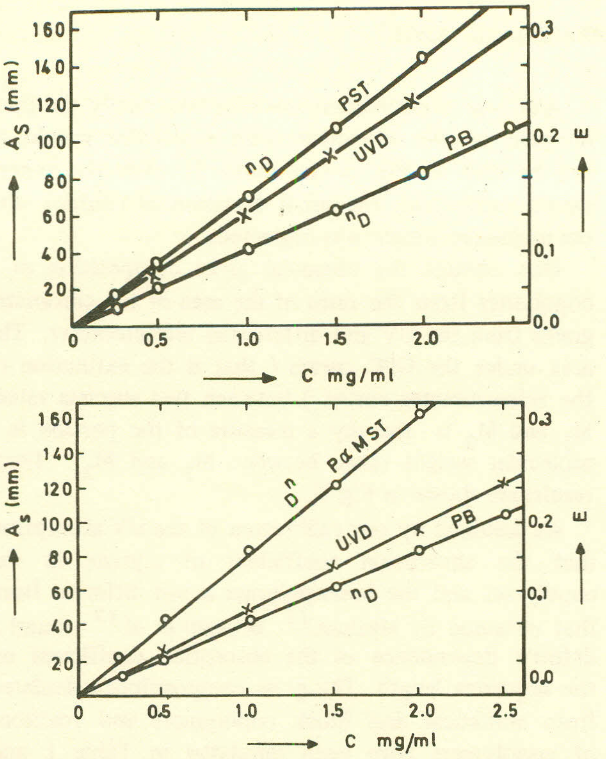

Fig. 3. Calibration of refractometer and UV instrument with homopolymers in tetrahydrofuran(THF)' (A). For polystyrene and polybutadiene (B). For poly α-methylstyrene and polybutadiene. Where n_D = Refractive index; UVD = UV detector; E = Extinction; A_s = recorder deflection.

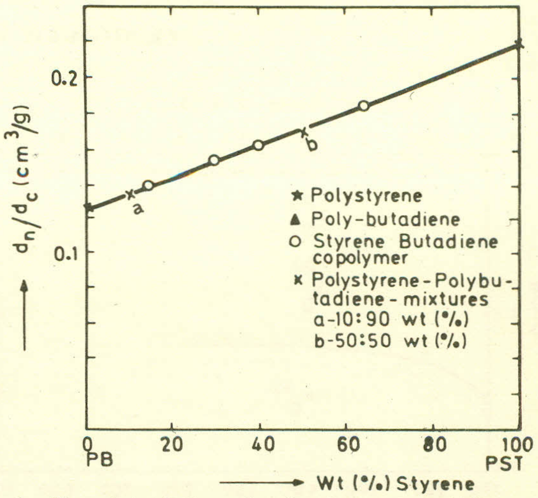

Fig. 4. The plot of the refraction increment (dn/dc) on the chemical composition of copolymers in THF., PB = Polybutadiene and PST is Polystyrene.

portions of the styrene-butadiene components in the copolymer respectively. Therefore, (dn/dc) measurements on homo and copolymers and mixtures from homopolymers (styrene and butadiene out of which the copolymer is composed) were carried-out with a differential refractometer at 25° and 40° The corresponding (dn/dc) values are plotted against the compositions of the copolymers in Fig. 4. Tetrahydrofuran (THF) was used as solvent, because we had used it as the elution medium for the GPC investigation. Fig. 4.

TABLE 1. CALCULATED CHEMICAL COMPOSITION OF STATISTICAL AND A BLOCK CO-POLYMER.

	GPC analysis weight %		IR - analysis weight %		NMR analysis weight %		Copolymer
	ST	BD	ST	BD	ST	BD	
SBR - 8	29,60	70,40	28,00	72,00	32,30	67,70	S-B-S
SBR - 1	31,30	69,80	29,00	71,00	31,90	68,10	–"–
SBR - 2	23,40	76.60	25,00	75,00	23,00	77,00	–"–
SBR - 4	25,50	74,50	23,00	77,00	–	–	–"–
F_2/SBR - 1	25,00	75,00	29,00	71,00	31,26	68,70	–"–
SBR - 9	14,50	85,50	13,80	86,20	12,20	87,80	statist.
SBR - 12	22,00	78,00	23,00	77,00	22,00	78,00	–"–
SBR - 10	32,90	67,10	29,70	70,30	29,50	70,40	–"–
SBR - 18	31,00	69,00	29,40	60,60	38,40	61,60	–"–
SBR - 11	69,30	30,70	64,50	35,50	65,90	34,20	–"–
SE - 45b	94,50	5,50	–	–	94.50	5,50	A-B
SE - 29b	71,00	29,00	–	–	77,50	22,50	–"–
SE - 25b	19,00	81,00	–	–	22,50	77,50	–"–
F_4/SBR - 1	33,00	67,00	–	–	–	–	S-B-S
F_7/SBR - 1	36,00	64,00	–	–	–	–	–"–

ST = Styrene, BD = Butadiene, F = Fraction.

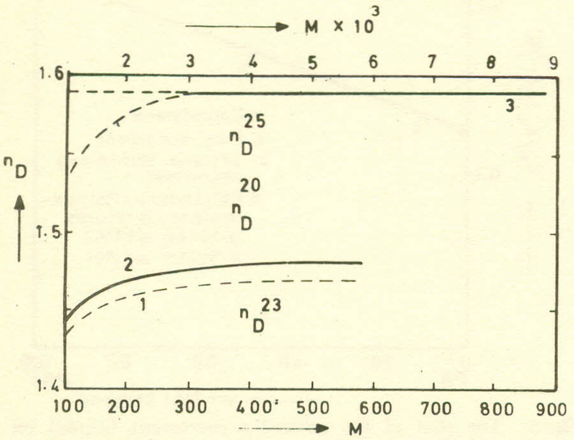

Fig. 5. Dependance of the refractive index(n_D) on the molecular weight of Polyethyleneglycol, ethylene oxide and polystyrene. Curve 1: Experimental data for poly-ethylene-glycol (Fred and Larsen[11]; Curve 2: Data for ethylene oxide from polymer hand book Vol. 34, 1966; Curve 3: Our data for polystyrene.

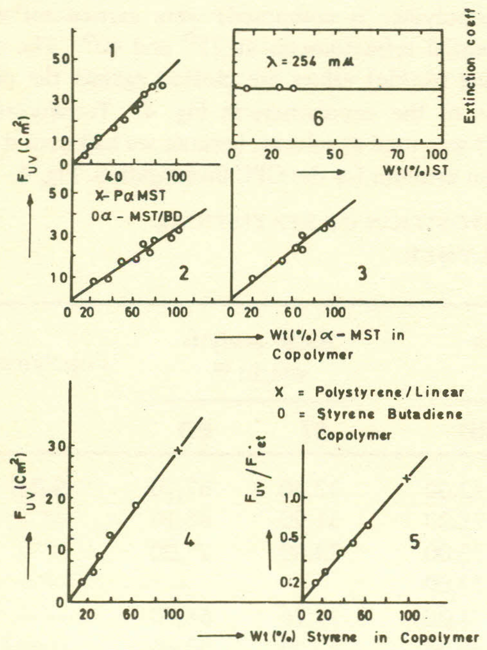

Fig. 6. Relations between the area (F) of a GPC curve and the composition of the copolymer at various column combinations Curve 1-4: Area from extinction curves; Curve 5: Area ratio (Extinction curve/refractometer); Curve 6: Extinction coefficient.

Polystyrene with a molecular weight $\overline{M}_w$ = 900 was also measured because the refraction increment shows a deviation from the constant value[11] at low molecular weight polymers, It indicates that a molecular weight dependance on the refraction increment occurs. According to Fred and Larsen,[11] the refractive index n_D depends on molecular weight as shown in Fig. 5.

Also our experimental investigations verify the poor increase of the refraction with molecular weight as can be seen in Fig. 5 (see curve 3). For the experiments carried-out, the small deviation of (dn/dc) with the molecular weight was neglected.

One obtains the chemical gross composition of a copolymer from the ratio of the area of the chromatograms from the UV and differential refractometer. The area under the GPC curves (that is the extinction or the refractometer curves) between two abscissa values M_1 and M_2 is thereby a measure of the portion in a molecular weight range between M_1 and M_2. These results are shown in Fig. 6.

We assumed by our calibration of the UV absorption that the absorption coefficient of styrene in the copolymer and the homopolymer is not different from that obtained by Meehan.[12] Brussau *et al.*[13] found a definite dependence of the absorption coefficient on the sequence length. The gross compositions calculated from statistical and block copolymers and fractions of copolymers have been tabulated in Table 1 and compared with the values obtained from IR and NMR.

References

1. J. Porath und P. Flodin, Nature, **183** (1957).
2. E. Ungerer, Kolloid Z., **36**, 228 (1925).
3. P. Flory, J.Am. Chem. Soc., **58**, 1877 (1936).
4. K.H. Altgelt, Makromolekulare Chemie, **88**, 75 (1965).
5. H. Determann *et al.*, Makromol. Chemie, **73**, 168 (1964).
6. W. Heitz *et al.*, Makromolekulare Chemie, **102**, 63 (1967).

7(a). Runyon, Barnes *et al.*, J. Appl. Polym.Sci., **13** (1969).
(b). Harmon and Folt, Rubber Chem. Tech., 449 (1973).
(c). J. M. Evans, Rubber and Plastics Reserch Assocation Members Journal July, 183 (1974).

8. H.J. Cantow, J. Probst und Ch. Stojanov, in Kautschuk und Gummi, Kunststoffe, **21**, 609 (1968).
9. Ch. Stojanov, Dissertationsarbeit, Freiburg i.Br. (1971).
10. E. Seiler, Dissertationsarbeit, Freiburg i.Br. (1970).
11. N. Fred und J. Larsen, J.Appl. Polymer Symposia, **8**, 111 (1969).
12. E.J. Meehan, J. Polymer Sci., **1** 3,375 (1946).
13. R.J. Brussau und D. Stein, Angewandte Makromolekulare Chemie, **168**, 12 (1970).