NOTE

Properties of Copolymers: Estimation and Prediction

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INTRODUCTION

Prediction of polymeric material properties, their correlation with their chemical structure, numerical estimation, and prediction from additive group contributions[1] is very important, especially in the case of copolymers obtained from two or more monomers. It is easy to calculate that from 1000 of a known kind of monomers we can obtain almost 10^6 types of copolymers and 10^9 types of terpolymers. Taking into account that each type of polymeric material has different properties depending on mutual proportions of monomeric units, it is almost impossible to test experimentally all of them without some previous prediction, based on knowledge of the properties of the respective homopolymers.

It seems very useful to start with some simplifications, connected with additive properties of groups enclosed in a copolymer molecule. It is also advantageous to use "monomer unit contributions" instead of "group contributions" as usual in such a procedure (for methyl, phenyl, or carbonyl group, etc.). This assumption is identical with using as a "monomer contribution" a property for homopolymer built from monomeric units present in the examined copolymer.

Such an approach was successfully applied by Fox[2-4] in the case of the estimation of the glass transition temperature for copolymers or homogenic polymer mixtures. In general form, the Fox equation can be written as

$$\frac{1}{T_{gc}} = \sum \frac{1}{T_{gi}} w_i \qquad (1)$$

where T_{gc} and T_{gi} are the glass transition temperature of the copolymer and the proper homopolymer, respectively. w_i is the weight fraction of monomeric units of type "i" (or the weight fraction of homopolymers in a homogenic mixture). Assuming that molar volume contributions are additive, a similar equation can be written:

$$\frac{1}{\rho_c} = \sum \frac{1}{\rho_i} w_i \qquad (2)$$

where ρ_c and ρ_i are the density of the copolymer and the proper homopolymer, respectively.

It is known[1] that a specific refractive increment dn/dc can be estimated via additive molar properties. However, for estimation of dn/dc, the following equation can be useful:

$$\left(\frac{dn}{dc}\right)_c = \sum \left(\frac{dn}{dc}\right)_i w_i \qquad (3)$$

where n is the refractive index, c is the weight concentration (in $g_{\text{polymer}}/g_{\text{solution}}$), and indexes c and i correspond to the copolymer and the i-type homopolymer, respectively.

Generally, using known properties of i-type homopolymers, a_i (for instance, $1/T_g$), we can predict a property of P_c. For a copolymer obtained from two type of monomers,

$$P_c = a_1 w_1 + a_2 w_2$$

$$w_1 + w_2 = 1 \qquad (4)$$

indicating that, assuming P_c, we can calculate the composition of the copolymer:

$$w_1 = \frac{P_c - a_2}{a_1 - a_2}$$

In the case of a terpolymer, we can assume the two properties P_c and Q_c, which leads to the set of equations
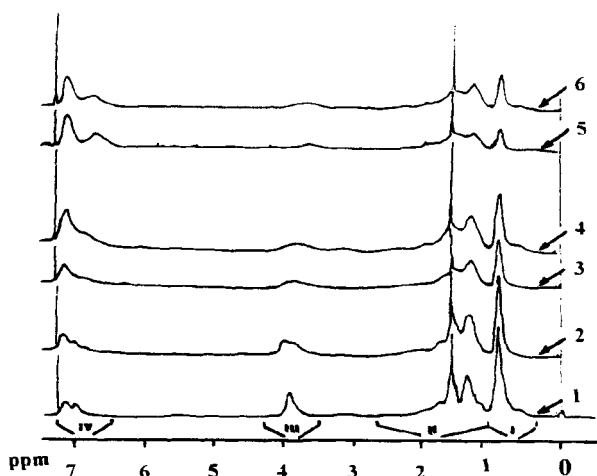
Figure 1   ¹H-NMR spectra of ST/BA/BM copolymers. Numbers as in Table I.

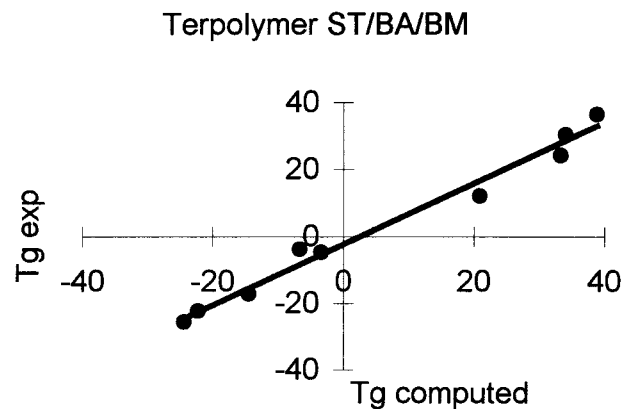$$P_c = a_1 w_1 + a_2 w_2 + a_3 w_3$$

$$Q_c = b_1 w_1 + b_2 w_2 + b_3 w_3$$

$$1 = w_1 + w_2 + w_3 \qquad (4a)$$

This approach can be generalized on an n-component system. In the presented article, this approach was checked using the example of two sets of terpolymers.
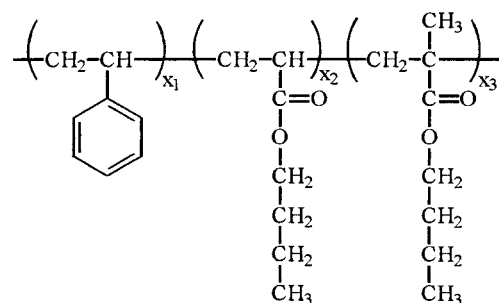
EXPERIMENTAL

The first set of terpolymers was obtained by radical copolymerization of styrene (S), butyl acrylate (BA),
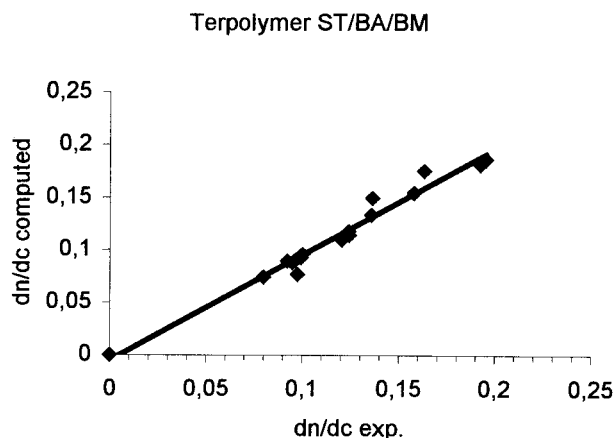

Figure 2   Correlation between experimental and computed T_g.

and butyl methacrylale (BM) at 80°C in bulk to 5–10% of conversion. AIBN was used as an initiator. The products were dissolved in chloroform, precipitated with ethanol, and dried under a vacuum. AIBN was used as an initiator. The chemical structure of the terpolymers obtained can be presented as follows:

Table I   Experimental Results for Terpolymers ST/BA/BM

No. Sample	w_1 (S)	w_2 (A)	w_3 (M)	dn/dc	T_g	ρ_{25}
II 1	0.18234	0.10201	0.71565	0.0904		1.0518
II 2	0.23870	0.47869	0.28261	0.0957		1.0378
II 3	0.34852	0.27866	0.37282	0.1139		1.0469
II 4	0.40368	0.18526	0.41105	0.1495		1.0529
II 5	0.52082	0.19328	0.2859	0.1544		1.0601
II 6	0.69095	0.05336	0.25569	0.1809		1.0575
III 1	0.15826	0.10896	0.73278	0.08966	24.1	1.0474
III 2	0.20293	0.40014	0.39694	0.08776	−4.8	1.0423
III 3	0.34215	0.23441	0.42344	0.118		1.0416
III 4	0.39958	0.18074	0.41968	0.1335	30.3	1.0504
III 5	0.54067	0.11563	0.34370	0.1751	36.4	1.0553
III 6	0.70424	0.02670	0.26906	0.1857		1.0382
IV 1	0.23970	0.5378	0.2214	0.09236	−17.3	1.0347
IV 2	0.24270	0.6564	0.101	0.0764	−25.8	—
IV 3	0.34950	0.4986	0.1519	0.1097	−4.0	1.0493
IV 4	0.13900	0.5805	0.2806	0.0739	−25.8	1.0387

Terpolymer ST/BA/BM

Figure 3 Correlation between experimental and computed values of dn/dc.

Terpolymer TBPM/BA/BM

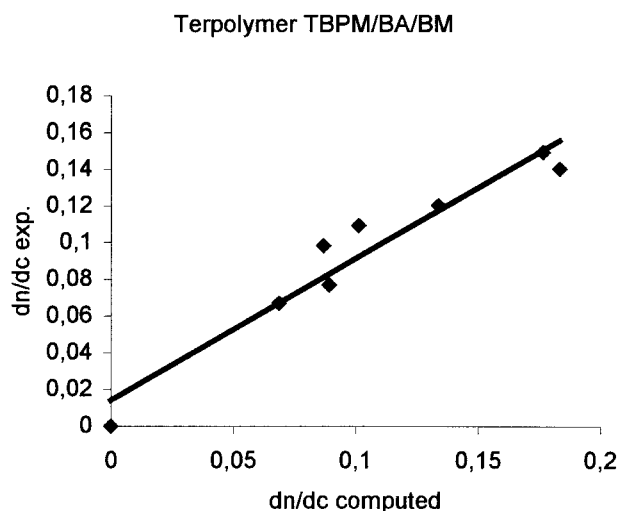**Figure 4** Correlation between experimental and computed values of dn/dc.

where x_1, x_2, and x_3 are the mol fractions of corresponding monomeric units.

The mol fractions were calculated from ^{1}H-NMR spectra. In Figure 1, NMR spectra for the terpolymers are presented. In the spectra appears four groups of picks: I, for protons in methyl groups; II, for methylene groups; III, for protons in the —O—CH_2— group; and IV, for aromatic protons. Taking into account the intensities of particular picks, it was possible to calculate mol fractions x_1, x_2, and x_3 and the weight fractions w_1, w_2, and w_3 of the corresponding monomeric units. The results are presented in Table I.

Refractive index increments were measured by the refractometry method for chloroform solutions at 25°C for 589.3 mμ. Concentration is expressed in $g/g_{solution}$.

Glass transition temperatures were determined using a differential scanning calorimeter DSC-7 of Perkin–Elmer, under nitrogen, at flow rate 25 cm^3/min and a heating rate 10°/min. Density was measured by the pycnometric method in 25°C. The results are presented in Table I.

Using the experimental values w_1, w_2, and w_3, according eqs. (1)–(3), the calculated values were computed and compared with the experimental data from

Table I. The results are presented in Figures 2 and 3. As we can see, a correlation between the experimental and computed data is quite good. Because the density of copolymers examined was in all cases almost the same (1.03–1.05), the relation presented by eq. (3) was not analyzed.

The next set of terpolymers was obtained from tribromophenyl methacrylate, BA, and BM by radical copolymerization in bulk, in conditions as in the first set. The chemical structure can be presented as follows:
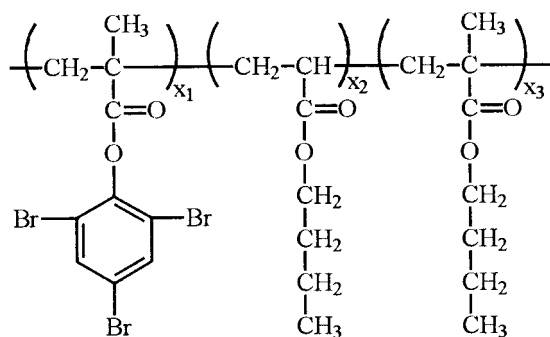
Table II Experimental Results for Terpolymers TBPM/BA/BM

Sample	w_1	w_2	w_3	dn/dc	T_g (°C)	ρ_{25}
I.1	0.865	0.086	0.018	0.140	91.6	—
I.2	0.127	0.778	0.096	0.067	—	1.096
I.3	0.168	0.096	0.736	0.098	—	1.124
I.4	0.320	0.486	0.195	0.071	−0.9	1.204
I.5	0.193	0.156	0.651	0.077	—	1.141
I.6	0.811	0.151	0.0378	0.149	—	1.520
I.7	0.522	0.257	0.221	0.120	43.9	1.332
PMTBP	1			0.206	160.4	2.144

Terpolymer TBPM/BA/BM
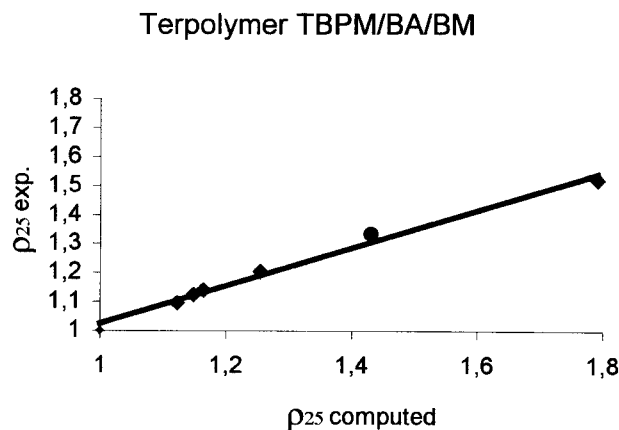
Figure 5   Correlation between measured density and computed values.

The terpolymers were analyzed by NMR, by a method similar to that described for the first set of experiments. Computed compositions as well as the results of density measurements and T_g and dn/dc data are presented in Table II. Correlations with the values computed according to eqs. (1)–(3) are presented in Figures 4 and 5.

Correlations with values computed according to eqs. (1)–(3) are presented in Figures 4 and 5. As we can see, the experimental error is ±0.02, but linear correlation

is satisfactory. In Figure 5, the experimental data of density measurements are compared with the computed data according eq. (2). As we can see, a good linear correlation was found. However, the experimental data are slightly lower than are the computed values. This can be a result of the inhomogeneity of the samples or the slight to high density of poly(tribromophenyl methacrylate) taken for the computation (2.144 g/cm^3), which was measured for a sample obtained by polymerization in bulk.

The results of the experiments failed to confirm our assumptions that using "monomer unit contributions" one can estimate the properties of copolymers. It seems that deviation from the additivity for multicomponent copolymers is smaller than that for dicomponent copolymers. For multicomponent copolymers, prediction of two or more properties is possible according to a set of equations similar to (4a). The method was found to be a convenient way for designing "tailor-made polymers."

REFERENCES

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2. Fox, T. G. Bull Am Phys Chem 1956, 1, 123.
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