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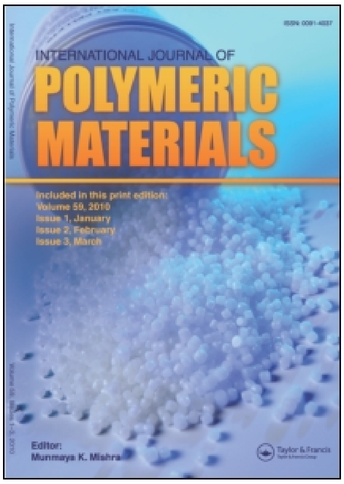

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On the Rheological Similarity of Physical Networks of Various Origin†

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It was established that the principle of temperature-time-concentration superposition for the solutions of styrene-based ionomers in DMPh is applicable for the dependences of storage modulus on temperature (20–100°C), frequency ($10^{-3}-1.5$ Hz), degree of neutralization (0–50 mol.%) and concentration (15–45 g/dl). This fact can be explained in terms of rheological similarity of physical networks connected with macromolecular chain entanglements and with salt group interactions. Some details of the model of concentrated polymer solutions are discussed.

According to a recent concept the rheodynamic properties of amorphous polymers and their solutions are determined mainly by the presence of one or several fluctuational networks.[1,2] We studied the contribution of such networks to the storage modulus G' of solutions of styrene-based ionomers.[3] Dimethyl phthalate (DMPh) was chosen as solvent.

The samples of ionomers were prepared by neutralization of the copolymers of styrene and acrylic acid.[3] They are designated as CP-mol.% of acrylic acid.mol.% of degree of neutralization. For example CP-4.20 indicates that the copolymer contains 4 mol.% of acrylic acid and its degree of neutralization is 20 mol.%. Both parameters were estimated by acidimetric titration. The degrees of polymerization were estimated by gel permeation chromatography.

The intrinsic viscosity ($[\eta]$) was measured in a standard Ubbelohde viscometer adapted for dilution. The G'-value measurements of the solutions were

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performed in modified Weissenberg rheogoniometer in the range of linear viscoelasticity at the frequencies from 10^{-3} to 1.5 Hz, temperatures from 20 to 100°C and concentrations from 15 to 45 g/dl.

There are two kinds of fluctuational networks in the system under investigation. In the first network knots are formed by entanglements of macromolecular chains. Such a network exists in all concentrated polymer solutions and polymer melts. In the second network knots are formed by salt group interactions. It can be proved by the analysis of the $[\eta]$-values of copolymers in various solvents. Let us compare the $[\eta]$-values of CP-4.0, its methylated derivative (CP-0.0) in which all the acrylic acid groups are replaced by ester groups, and CP-4.25 (Table I).

TABLE I

The $[\eta]$-values (dl/g) of copolymers, degree of polymerization 10^4

Solvent	CP-4.0	CP-0.0	CP-4.25
Toluene	1.15	2.5	
Tetrahydrofuran (THF)	2.5	2.6	2.2
DMPh	1.25	1.3	1.1

The ratio between the $[\eta]$-values of CP-4.0 and CP-0.0 in toluene is more than two because of H-bonds between acrylic acid groups in CP-4.0. The $[\eta]$-values in THF are equal because this solvent destroys the polymer–polymer H-bonds. The $[\eta]$-values of both copolymers in DMPh are also equal, indicating that DMPh destroys the polymer–polymer H-bonds. The low absolute $[\eta]$-values in this solvent are explained by the poor thermodynamic solvent quality of DMPh. The presence of sodium acrylate groups (CP-4.25) decreases the $[\eta]$-values both in THF and in DMPh due to additional interactions between these groups.

The main purpose of this investigation was to establish the dependence of the G'-values on the specific interactions of sodium acrylate groups. This necessitates all the variables (temperature, concentration) to be excluded by the superposition method.

Proceeding with the temperature-time superposition requires[4] the data to be presented in reduced variables:

$$G'_r = G'(T/T_0) \quad \text{and} \quad \omega_r = \omega(\eta T_0/\eta_0 T),$$

where T is the temperature of experiment, T_0 the reference temperature, η and η_0 the Newtonian viscosities at T and T_0. An example of this superposition is shown in Figure 1 for solutions of CP-4.50 of various concentrations and for the concentration of 42 g/dl of various degrees of neutralization. It is obvious that the superposition method applies in all the cases. It is

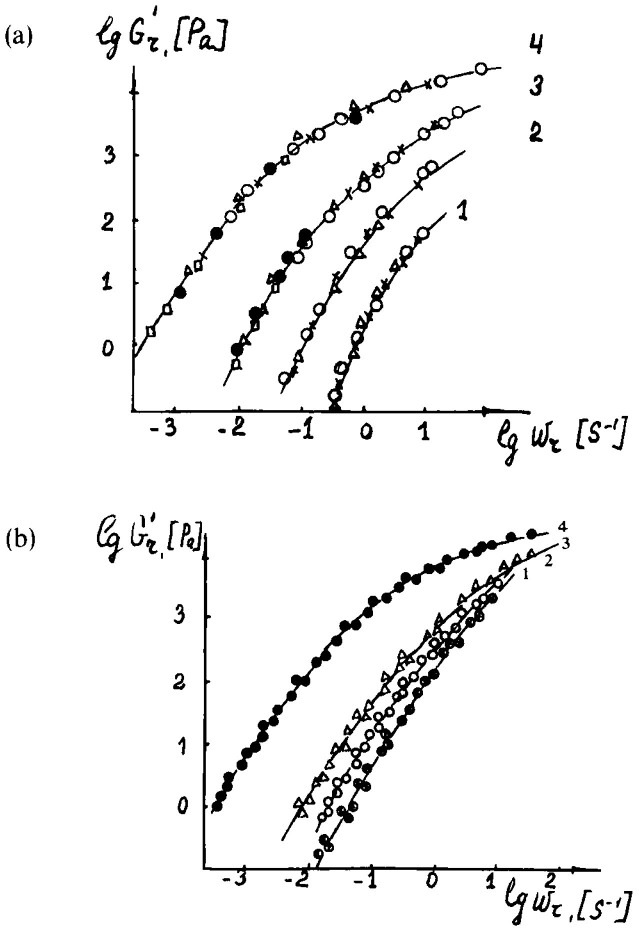

FIGURE 1 The dependences of storage modulus on frequency for solutions of CP-4.50 at various concentrations (a) and for copolymer concentration of 42 g/dl at various degrees of neutralization (b) in DMPh. Reference temperature = 30°C. (a) (1) 16 g/dl, (2) 20 g/dl, (3) 30 g/dl, (4) 42 g/dl. (b) (1) CP-4.0, (2) CP-4.6, (3) CP-4.20, (4) CP-4.50.

interesting to note that the increase in G'-values with concentration or degree of neutralization is less pronounced in the high frequency range. It may be explained by the analysis of the time relaxation spectra of the systems (Figure 2). The increase in the degree of neutralization as well as the increase in concentration leads to the appearance of relaxators with the long time of relaxation. When the high frequency forces are applied to the system, the long time part of the time relaxation spectrum is cut off,[1] but the lower are the concentration or degree of neutralization the less pronounced is this effect. This explains the disappearance of the difference between these various systems.

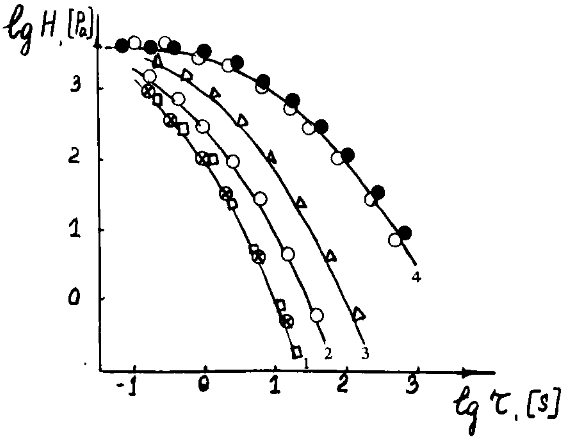

FIGURE 2 The spectra of time relaxation for the solutions of CP-4.50. (1) 16 g/dl, (2) 20 g/dl, (3) 30 g/dl, (4) 42 g/dl.

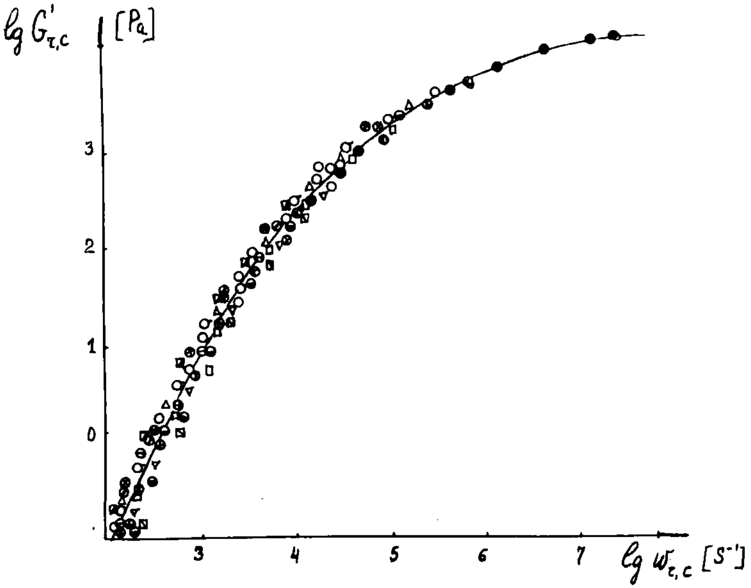

FIGURE 3 The storage modulus master curve for copolymer solutions in DMPH, Reference temperature = 30°C, reference concentration = 30 g/dl. (⬘) CP-4.0, 20 g/dl; (⊘) CP-4.20, 20 g/dl; (◒) CP-4.0, 25 g/dl; (▽) CP-4.0, 30 g/dl; (□) CP-4.20, 30 g/dl; (○) CP-4.0, 42 g/dl; (⊗) CP-4.20, 42 g/dl; (◩) CP-4.6, 20 g/dl; (⬙) CP-4.50, 20 g/dl; (⊛) CP-4.50, 25 g/dl; (◇) CP-4.6, 30 g/dl; (⊕) CP-4.50; 30 g/dl; (△) CP-4.6, 42 g/dl; (●) CP-4.50, 42 g/dl.

The applicability of the superposition method indicates the absence of the microphase separation in our systems. This separation was observed for the melts of ethylene based ionomers.[5]

The next step was to use de Witt's method[6] of concentration superposition for our data. In this method the reduced variables are:

$$G'_{r,c} = G'_r(c_0/c) \quad \text{and} \quad \omega_{r,c} = \omega_r(c_0/c)\eta,$$

where c is the current concentration and c_0 the reference one. The data for all the systems over the whole range of temperatures and frequencies fall on the same master curve (Figure 3). This result can be explained in terms of a superposition of two physical networks, the first of them being caused by macromolecular chain entanglements and the second by interactions of salt groups. Therefore these networks, although of different physical origin, are rheologically similar. This means that the real entanglements play a minor role in the rheological behaviour of concentrated polymer solutions. The term "entanglement" should be understood as just a partial superposition of macromolecular coils of kinetic rather than of morphological origin.

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