"ELASTIC RECOIL" IN POLYMER SOLUTIONS AS A FUNCTION OF CONCENTRATION

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The critical concentration C_c corresponding to formation of a continuous structural network was determined as a measure of "elastic recoil" in polymer solutions. It was shown that C_c is not related to deformation parameters but reflects the transition from one molecular-kinetic state to another in the material under investigation.

Highly elastic deformations in polymer solutions, which are measured from the "elastic recoil" [1], are associated with structural deformations, which are assumed to have the form of continuous three-dimensional structures consisting of macromolecules or groups of macromolecules. Action of an external mechanical factor leads to a conformational change in the structure-forming macromolecules and to partial or complete destruction of the structure. This is reflected primarily in the high-elasticity parameters of polymer systems and is readily picked up by measuring the "elastic recoil" γ_e.

That the elasticity of changes in the shape of a polymer solution results from formation of a continuous structural network follows from measurements of the "elastic recoil" as a function of concentration for various polymer solutions. We measured this quantity in solutions of polystyrene in benzene and polyvinyltoluoul in n-xylol, using an elastoviscosimeter [2], which permits determination of the "elastic recoil." We did not detect "elastic recoil" during shear deformation in the solutions investigated until the concentration C reached a certain critical level C_c (Fig. 1a and b). In this case, the macromolecules or macromolecular associates apparently do not form a continuous structural network, while the separate macromolecules and aggregates, which are themselves elastic, cannot cause elasticity of changes in shape for the solution as a whole after application of external force ceases. Actually, the individual macromolecules and aggregates undergo an elastic change in shape, but their centers of symmetry remain stationary if Brownian motion is not taken into account. In this case, solvent flows develop around the macromolecules, but these cancel one another because of the enormous number of macromolecules and aggregates present and their effect in altering the shape of even a microscopic volume is absolutely nil. At a definite concentration C_c (Fig. 1), the density of macromolecules reaches a level that permits existence of structures that are continuous and extend throughout the solution volume. Since they are themselves elastic, these structures provide elasticity for changes in the shape of the solution as a whole. "Elastic recoil" is observed at concentrations above a certain critical C_c. Graphs representing the "elastic recoil" determined under a steady-state flow regime as a function of the logarithm of the solution concentration

TABLE 1. Comparison of Critical Concentrations C_c

Polymer	Solvent	Molecular mass of polymer $\bar{M}_v$	Critical concentration C_c, wt.%		
			from "elastic recoil"	from viscosity [3, 4]	theoretical calculation [3, 4]
Polystyrene	Benzene	$7{,}0 \cdot 10^4$	13,5	19	18
Polystyrene	Benzene	$4{,}9 \cdot 10^5$	2,6	2,5	–
Toluol	Paraxylol	$4{,}2 \cdot 10^5$	9,7	9,2	–

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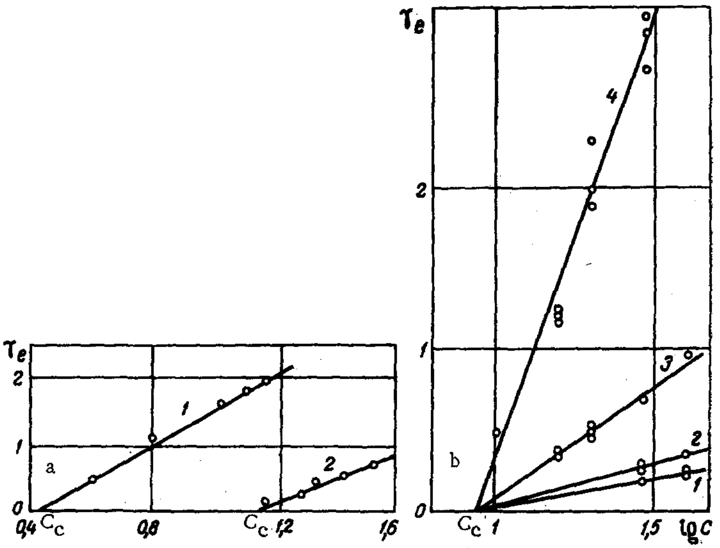

Fig. 1. "Elastic recoil" of solutions: a) of polystyrene in benzene as a function of concentration (γ_e – log C) with deformation rate $\gamma = 15.7\ \text{sec}^{-1}$: 1) PS with $\overline{M}_v = 7 \cdot 10^4$; 2) PS with $\overline{M}_v = 4.9 \cdot 10^5$, 20°C; b) of polyvinyltoluol in n-xylol as a function of concentration at 35° ($\overline{M}_v = 4.2 \cdot 10^5$); 1-4) deformation rates γ of 0.627, 3.14, 15.7, and 78.7 sec^{-1} respectively.

(γ_e –log C) are straight lines in the region of concentrations not greatly exceeding C_c. This makes it possible to find the critical concentration C_c by extrapolation (Fig. 1a and b).

The concentration corresponding to formation of a continuous structural network can be determined from the change in the dependence of solution viscosity on concentration [3], as well as from the change in the specific surface of a polymer aerosol (found from low-temperature krypton adsorption) with increasing initial-solution concentration [4]; roughly the same values are found to correspond to formation of a continuous structure in the solution in question as when they are determined from "elastic recoil" measurements. Table 1 gives a comparison of the critical concentration C_c found by these three methods; as can be seen, there is rather good agreement among them.

It is especially interesting that the critical concentration C_c is independent of the rate at which the test material is deformed before the "elastic recoil" is measured, i.e., the γ_e –log C curves are extrapolated to the same point C_c regardless of the deformation rate at which the "elastic recoil" versus concentration curve was determined. This is illustrated by Fig. 1b, which shows that the critical concentration C_c determined from "elastic recoil" measurements is not related to the deformation parameters but reflects a transition from one molecular-kinetic state to another in the test material. We can therefore use C_c to determine the parameters characterizing this state.

NOTATION

γ_e	"elastic recoil";
C_c	critical concentration for formation of continuous structural network in polymer solutions;
$\overline{M}_v$	molecular mass (from characteristic viscosity measurements).

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