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Application of the Theory of Dilute Polymer Solutions to the Assessment of the Structure and Properties of Styrene–Acrylic Acid Copolymers

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Abstract—Properties of dilute solutions of polystyrene and styrene–acrylic acid copolymers in DMF and ethyl acetate were studied in the temperature range 20–35°C. It was shown that the dependences of the intrinsic viscosity and Huggins constants on temperature for the copolymers differ from that for polystyrene. Comparison of the "quality" of the solvents was carried out.

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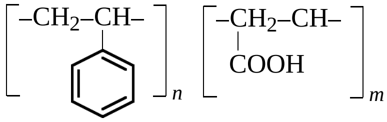
At present one of the actual directions of the polymer chemistry is synthesis of polymers for medicine and biology. Nikolaeva [1] performed a multistep transformation of copolymers of styrene with allyl alcohol to modified polymers containing porphyrin derivatives in the side chain. Such fragments impart to materials biological, photochemical, and catalytic activity. The transformation involves polymer-analogous processes and is carried out in solution. These is no doubt that the properties of the solution, polymer–solvent interactions, and the "quality" of the solvent, by which is meant the thermodynamic affinity between the polymer and solvent, contribute to the reaction progress. Therewith, the higher the intrinsic viscosity and the lower Huggins constant, the "better" is the solvent. In a "good" solvent, the molecular clew is better loosened than in "bad."

In the present work we took as objects for study styrene–acrylic acid copolymers **I** prepared by suspension polymerization at monomer weight ratios of 1 : 1, 1 : 2, 2 : 1, and 3 : 1.


(1)

Characteristics of the starting copolymers and suspension polystyrene taken as reference are presented in Table 1.

Note that the composition of the copolymer does not correspond to the composition of the starting mixture of monomers, which, however, would be expected in view of the copolymerization constants [2]. At the same time, the general trend is that an increase in the fraction of acrylic acid in the starting monomers increases the fraction of its chain members in the copolymers. As shown in [1], in view of the large size

Table 1. Characteristics of polystyrene and styrene–acrylic acid copolymers

Run no.	Starting styrene : acrylic acid weight ratio	Composition of polymer (styrene : acrylic acid), wt%		Molecular weight, amu
		wt%	mol%	
1	0	100	100	22600
2	3 : 1	97.5 : 2.5	26.9 : 1	7650
3	2 : 1	96.4 : 3.6	18.6 : 1	5840
4	1 : 1	90.3 : 9.7	6.7 : 1	4900
5	1 : 2	86.7 : 13.3	4.6 : 1	3830

Table 2. Effect of temperature on the rheologic characteristics of dilute solutions of polystyrene and styrene–acrylic acid copolymers in DMF and ethyl acetate.

t, °C	Styrene : acrilic acid weight ratio	DMF		Ethyl acetate	
		$[\eta]$	K_H	$[\eta]$	K_H
20	3 : 1	0.103±0.004	2.957±0.480	0.105±0.002	2.563±0.150
25		0.095±0.009	3.397±1.285	0.093±0.002	5.896±1.142
30		0.096±0.009	3.874±1.718	0.068±0.020	3.874±2.748
35		0.083±0.007	6.914±1.501	0.081±0.014	6.914±1.107
20	2 : 1	0.085±0.005	5.909±1.285	0.105±0.002	0.909±0.082
25		0.084±0.008	4.236±1.080	0.086±0.002	2.115±0.901
30		0.089±0.002	3.138±0.525	0.069±0.009	5.664±0.023
35		0.069±0.007	10.080±2.008	0.060±0.021	8.560±1.151
20	1 : 1	0.063±0.017	30.097±4.250	0.090±0.005	2.695±0.082
25		0.074±0.004	11.836±2.354	0.083±0.004	4.292±1.982
30		0.052±0.012	41.621±3.608	0.037±0.020	63.820±7.201
35		0.046±0.011	50.366±3.280	0.045±0.010	29.410±3.983
20	1 : 2	0.075±0.006	22.672±2.870	0.082±0.002	1.986±0.821
25		0.082±0.006	15.230±2.150	0.081±0.008	2.745±0.280
30		0.083±0.002	10.637±1.857	0.070±0.010	5.606±2.007
35		0.067±0.003	28.869±2.505	0.057±0.012	11.048±2.020
20	polystyrene	0.158±0.009	2.461±1.025	0.101±0.003	3.353±1.008
25		0.153±0.002	2.498±1.356	0.099±0.005	4.032±1.200
30		0.137±0.002	3.560±0.853	0.079±0.018	6.538±2.050
35		0.123±0.005	4.190±1.282	0.073±0.021	9.306±2.871

of the porphyrin fragment, it is expedient to have in the modified polymer 1–2 tetrapyrrole fragments per 100 elementary units of the macromolecular chain. Therefore, there is no need to further increase in the number of acrylic acid units in the copolymer.

Table 2 lists parameters of dilute solutions of the copolymers, intrinsic viscosity η and Huggins constant K_H, as functions of temperature and polymer composition.

As known, η is correlated with hydrodynamic flow resistance, which for a homopolymer, namely polystyrene, dissolved in DMF will be higher than for polystyrene dissolved in ethyl acetate. As the temperature increases, the hydrodynamic flow resistance decreases (Fig. 1). On the whole the resulting data provide evidence for data for styrene–allyl alcohol copolymers [3].

The difference in the $[\eta]$ values for polystyrene solutions in DMF, obtained by us and reported in [3], is associated with the lower molecular weight of our polystyrene sample. In terms of "quality," DMF is a better solvent for polystyrene than ethyl acetate.

The strength of polystyrene–solvent interactions is illustrated by K_H. In DMF this value smoothly grows with temperature, while in ethyl acetate it changes in a different way (Fig. 2).

On the whole both η and K_H show that the "quality" of DMF and ethyl acetate decreases with temperature. The fact that $[\eta]$ decreases with temperature suggests that the macromolecular clew in DMF and ethyl acetate swells weaker, and the thermodynamic affinity of the solvent to polymer decreases. Such behavior is characteristic of systems with a lower critical solution temperature.

The dependences of $[\eta]$ and K_H on temperature for the copolymers differ from those observed for the homopolymer (Figs. 3 and 6). This fact provides evidence in favor of individuality of the copolymers obtained.

In [3] we explained an analogous difference for the styrene–allyl alcohol copolymer by a nonuniform distribution of allyl alcohol units along the polymer chain. Such explanation cannot be accepted in this work, because the experiments were carried out with the same polymer sample over the entire temperature range. As the fraction of acrylic acid units in the copolymer increases, the $[\eta] = f(t)$ dependence gradually transforms from a decreasing exponent to a

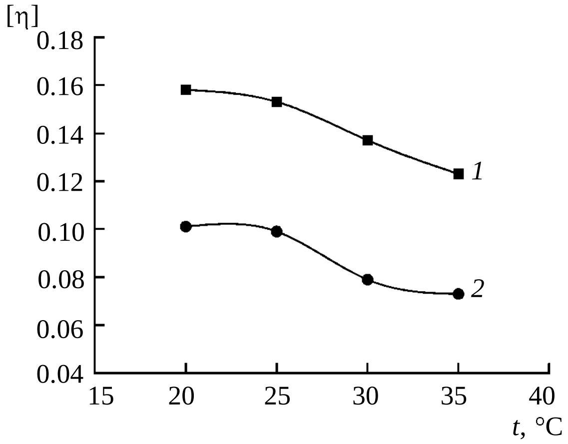


Fig. 1. Plots of intrinsic viscosity [η] vs. temperature *t* for polystyrene solutions in (*1*) DMF and (*2*) ethyl acetate.

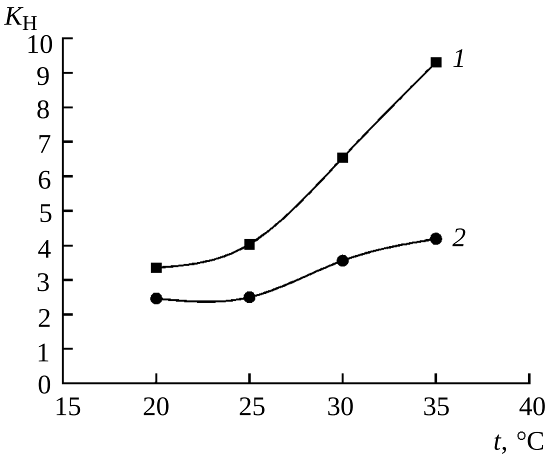


Fig. 2. Plots of Huggins constant K_H vs. temperature *t* for polystyrene solutions in (*1*) DMF and (*2*) ethyl acetate.

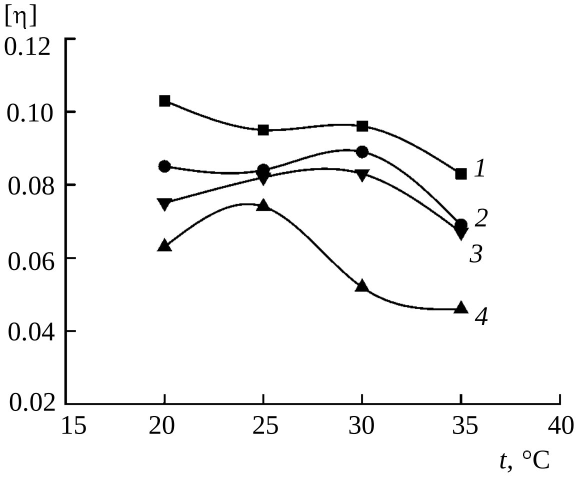


Fig. 3. Plots of intrinsic viscosity [η] vs. temperature *t* for solutions of styrene–acrylic acid copolymers in DMF. Styrene : acrylic acid weight ratio: (*1*) 3 : 1, (*2*) 2 : 1, (*3*) 1 : 2, and (*4*) 1 : 1.

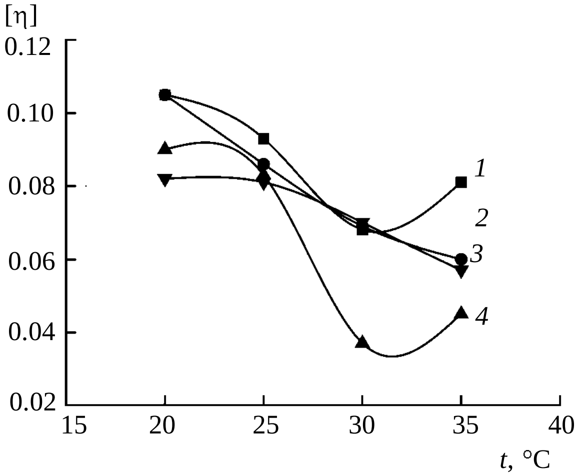


Fig. 4. Plots of intrinsic viscosity [η] vs. temperature *t* for solutions of styrene–acrylic acid copolymers in ethyl acetate. Styrene : acrylic acid weight ratio: (*1*) 3 : 1, (*2*) 2 : 1, (*3*) 1 : 2, and (*4*) 1 : 1.

function with a well-defined extremum (Figs. 3 and 4). These findings show that increasing content of acrylic acid units in the copolymer favors transition from the systems with a lower critical solution temperature to systems with higher and lower critical solution temperatures, on account of the fact that the macromolecular clew shrinks both with increasing and decreasing temperature. Since in dilute solutions solute–solute interactions are absent, this effect can hardly be considered in some other way.

Note, that ethyl acetate is a worse solvent for the homopolymer but a "better" solvent for the copolymers (its [η] is higher). The $[\eta] = f(t)$ dependences in DMF transformed in curves with maxima (Fig. 3), while in ethyl acetate the tendency for transfer to curves with minima is observed (Fig. 4). Note also that, as the content of acrylic acid units in the copolymer increases, the "quality" of ethyl acetate worsens to a lower extent compared to toluene [3].

Figures 7 and 8 show the plots of [η] on the content of acrylic acid units. These dependences are quite arbitrary because of different molecular weights of the copolymer samples used.

The presented data provide certain evidence for the absence of clear correlation between the solubility parameters of liquids and polymers. For example, the

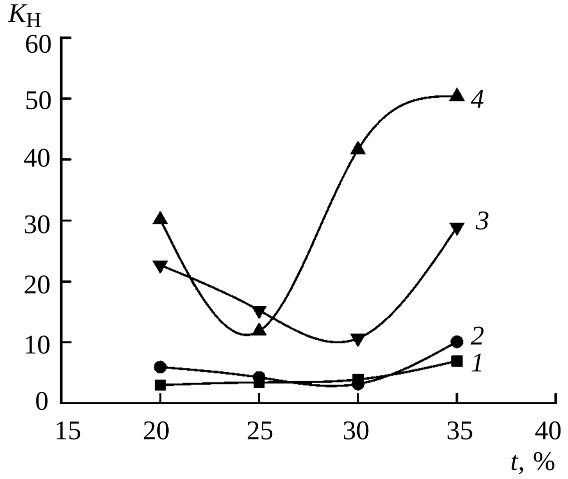


Fig. 5. Plots of Huggins constant K_H vs. temperature t for solutions of styrene–acrylic acid copolymers in DMF. Styrene : acrylic acid weight ratio: (*1*) 3 : 1, (*2*) 2 : 1, (*3*) 1 : 2, and (*4*) 1 : 1.

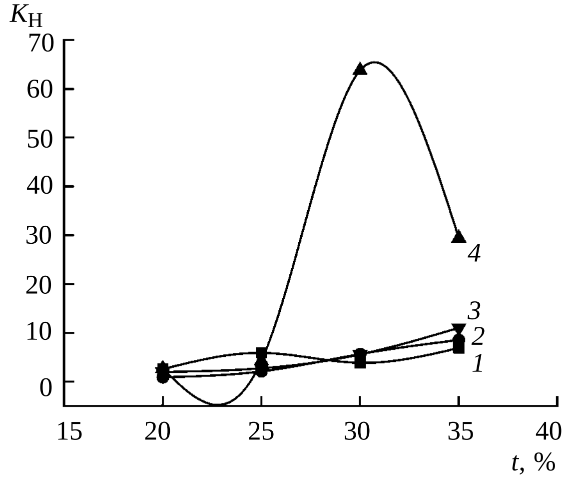


Fig. 6. Plots of Huggins constant K_H vs. temperature t for solutions of styrene–acrylic acid copolymers in ethyl acetate. Styrene : acrylic acid weight ratio: (*1*) 3 : 1, (*2*) 2 : 1, (*3*) 1 : 2, and (*4*) 1 : 1.

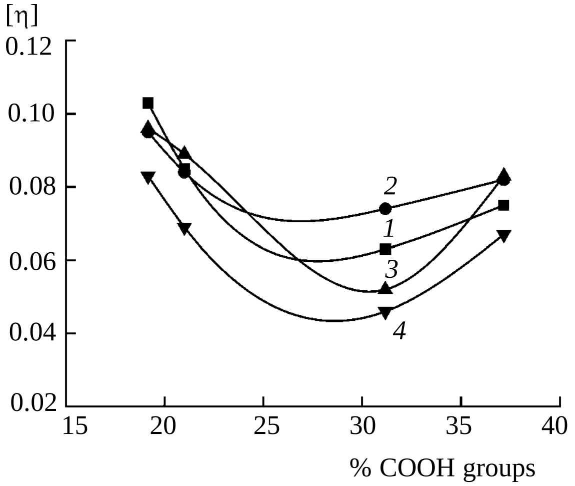


Fig. 7. Plots of intrinsic viscosity [η] vs. content of carboxy groups for solutions of copolymers in DMF. Temperature, °C: (*1*) 20, (*2*) 25, (*3*) 30, and (*4*) 35.

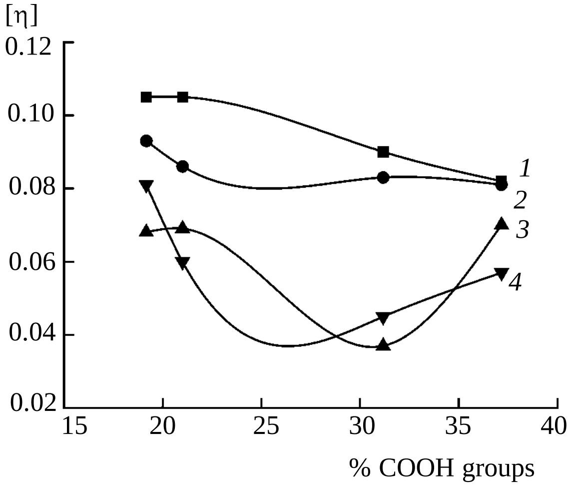


Fig. 8. Plots of intrinsic viscosity [η] vs. content of carboxy groups for solutions of copolymers in ethyl acetate. Temperature, °C: (*1*) 20, (*2*) 25, (*3*) 30, and (*4*) 35.

solubility parameter δ, $(\mathrm{J\,m^{-3}})^{0.5}$, for polystyrene is 18.2×10^3, for DMF 24.2×10^3, and for ethyl acetate 18.2×10^3 [4].

The obtained $[\eta] = f(t)$ and $K_H = f(t)$ functions allow us to suggest appropriate temperature conditions for polymer-analogous transformations involving acrylic acid units, at which the macromolecular clew will be stronger loosened. Evidently, under these conditions the functional groups will be more accessible. The chemical transformation in itself will surely also depend on other factors, such as the activation energy of the reaction. However, the tightness of the macromolecular clew and its permeability should also contribute something to the degree of transformation of the functional groups.

EXPERIMENTAL

The intrinsic viscosities [η] of the solutions of polymers were measured by the traditional dilution procedure in an Ubbelohde viscometer [5]. The polymer, 0.1 ± 0.00002 g, was placed in a calibrated 10-ml picnometer and dissolved in ethyl acetate or DMF at room temperature. The resulting solution was placed in the Ubbelohde viscometer and thermostated for

15 min at a specified temperature (20, 25, 30, or 35°C). After that the first measurement of the solution efflux time was carried out. The first portion of ethyl acetate or DMF, preliminarily weighed on analytical balances, was then added. The solution was stirred, thermostated for 15 min, and the second measurement of the efflux time was carried out. The further three efflux time measurements were carried out analogously. The relative viscosity was calculated by the formula

$$\eta_{\mathrm{rel}} = \tau_i/\tau_0,$$

where τ_i is the efflux time of the solution at definite dilution and τ_0, efflux time of the straight solvent.

The specific viscosity was calculated by the formula

$$\eta_{\mathrm{sp}} = \eta_{\mathrm{rel}} - 1.$$

From the resulting data, the η_{sp}/c ratio was calculated, where c is the concentration of the solution in g/100 g solvent. From the $\eta/c = f(c)$ dependences treated by the least-squares method, the intrinsic viscosities η and Huggins constants K_{H} were found by the formula

$$K_{\mathrm{H}} = \tan\alpha/[\eta]^2,$$

where $\tan\alpha$ is the slope of the straight line $\eta_{\mathrm{sp}}/c = f(c)$.

The composition of the copolymers was calculated from the carboxyl titration data in DMF [6].

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REFERENCES

1. Nikolaeva, O.I., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 2005.
2. *Fizika i khimiya voloknoobrazuyushchikh polimerov* (Physics and Chemistry of Fiber-forming Polymers), Mel’nikov, B.N., Ed., Ivanovo: IGKhTU, 2005.
3. Nikolaeva O.I., Usacheva T.S., Ageeva T.A., and Koifman, O.I., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2006, vol. 49, no. 6, p. 46.
4. Semchikov, Yu.D., *Vysokomolekulyarnye soedieniya* (Macromolecular Compounds), Nizhny Novgorod: Akademiya, 2003, p. 368.
5. Voyutskii, S.S., *Rasyvory vysokomolekulyarnykh soedinenii* (Solutions of Macromolecular Compounds), Moscow: Goskhimizdat, 1960, p. 132.
6. Toroptseva, A.M., Belogorodskaya, K.V., and Bondarenko, V.M., *Laboratornyi praktikum po khimii i tekhnologii vysokomolekulyarnykh soedinenii* (Laboratory Manual on the Chemistry and Technology of Macromolecular Compounds), Leningrad: Khimiya, 1972, p. 416.