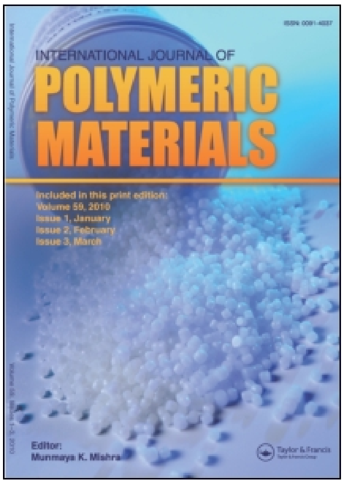

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S. V. Kolesov[a]; E. I. Kulish[a]; G. E. Zaikov[a]; K. S. Minsker[a]
[a] Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

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Structural-physical Effects at Thermal Degradation of PVC in Complex Objects

S.V. KOLESOV, E.I. KULISH, G.E. ZAIKOV* and K.S. MINSKER

Institute of Biochemical Physics, Russian Academy of Sciences,
Moscow, Russia

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The influence of structure formation on thermodegradation of PVC in complex polymer objects is considered in the article. It was shown that structural-physical states of polymer mixtures simply depend on the method of obtaining a composite and affinity of polymers. Composites of the same composition may be obtained, which possess rather different dehydrochlorination rates for polyvinylchloride.

Keywords: PVC; thermal degradation; polymer structure; polymer mixtures

RESULTS AND DISCUSSION

Chemical behavior of polymers is generally defined by their structural-physical inhomogeneity: homogeneity of a polymer system, its state (solution, solid...), existence of associates of macromolecules and supermolecular formations, *etc.* For degradation of PVC and its mixtures with other polymers it was shown that in assembly with the factors defining stability of macromolecules – chemical structure of polymer chains, existence of low-molecular additives, solvent [1, 2] – structural-physical effects, association in solutions, in particular, provide a variety and complexity of kinetic regularities of polymer chain degradation. Association of macromolecules appearing at

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*Corresponding author.

concentration of diluted solutions of polymers is accompanied by solvent substitution in the macromolecular coil volume by monomeric chains of neighbor macromolecules with corresponding growth of local density of chains in the coil. Such structural transition, when the system transits from homogeneously distributed macromolecular coils to a system of associates of polymer molecules, is accompanied by a jump-like change of viscosity [3]. For PVC solutions in cyclohexanone (CHN) and 1,2,3-trichloropropane (TCP) it was shown [4] that the beginning of association corresponds to PVC concentrations of 0.9 mass% in CHN and 0.6 mass% in TCP. This is accompanied by the corresponding change in the rate of PVC decomposition (Fig. 1, curves 1, 2).

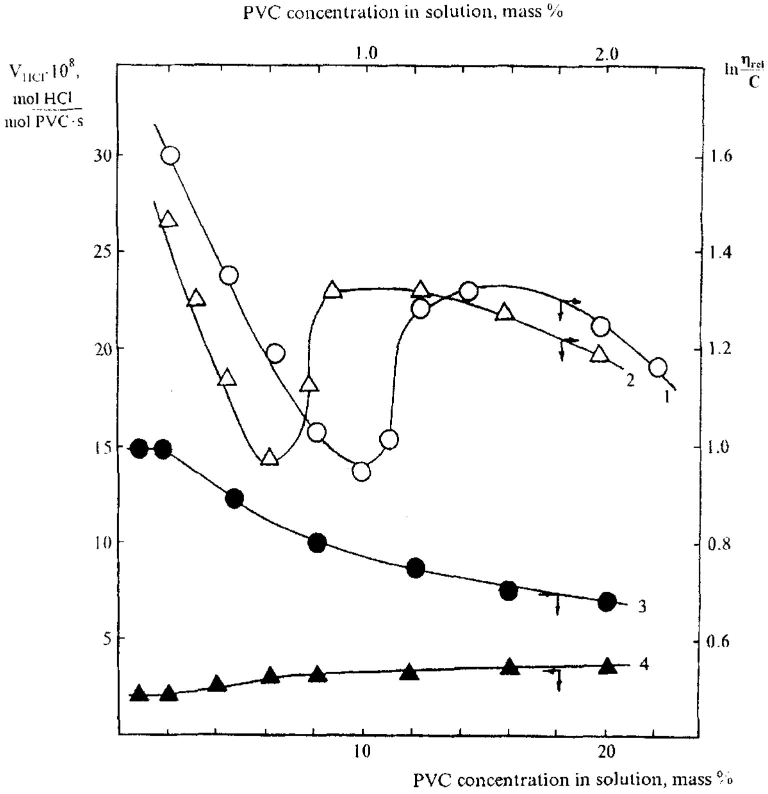

FIGURE 1 Dependency of the logarithm of reduced viscosity of solutions (1, 2) and the rate of PVC thermal dehydrochlorination (3, 4) on PVC concentration in CHN (1, 3) and TCP (2, 4) solutions at 423 K.

If the rate of dehydrochlorination remains constant in the concentration ranges, in which PVC exists as isolated macromolecules, then after an increase of concentrations up to values corresponding to the beginning of macromolecule association the rate of PVC degradation begins to change, decreasing in CHN and increasing in TCP (Fig. 1, curve 3, 4). The difference in the rates of PVC degradation in the present solvents is bound to different values of the basicity index B for CHN and TCP [2]. However, the fact that due to concentration of the PVC solution the rates of its decomposition in the absence of a solvent testifies the structurization of PVC with formation of a fluctuation network, consisting of dense aggregates, the supermolecular structure of which is similar to the PVC structure in block.

PVC macromolecules may be transferred into associated and aggregated state and, consequently, a change of the degradation rate may be caused not only by a change of concentration of a polymer solution, but also by addition of second polymer with low thermodynamic affinity to PVC. As an example, the following polymers relate to this class: polymethylmethacrylate (PMMA) and polystyrene (PS). The dependency "polymer solution visocity – mixture concentration" for solutions of polymer mixtures clearly shows (Figs. 2 and 3) that the presence of a second polymer (PMMA, PS) in the PVC-solvent system causes association of macromolecules in the range of solution concentrations, in which PVC is not yet associated. The increase of polymer-precipitator content causes a shift of the polymer solution concentration, at which the transition into the associated state happens, to the side of lower values.

Chemical influence of PMMA and PS on the decay of PVC is well-known [4]. At associated degradation with PVC they are depolymerized forming the monomers, which inhibit PVC decay in absence of a solvent during degradation. It was shown for the PVC-PMMA system that the monomer action reverses in solution [5], *i.e.*, the rate of PVC dehydrochlorination increases that should be also expected for the PVC-PS systems due to similarity of the systems. Let us note that for the study of PVC degradation rate in mixtures in solution the solutions of polymers were selected with the concentration showing the presence of macromolecule associates (2 mass %). The presence of extremes in the change of PVC dehydrochlorination rate in CHN and the

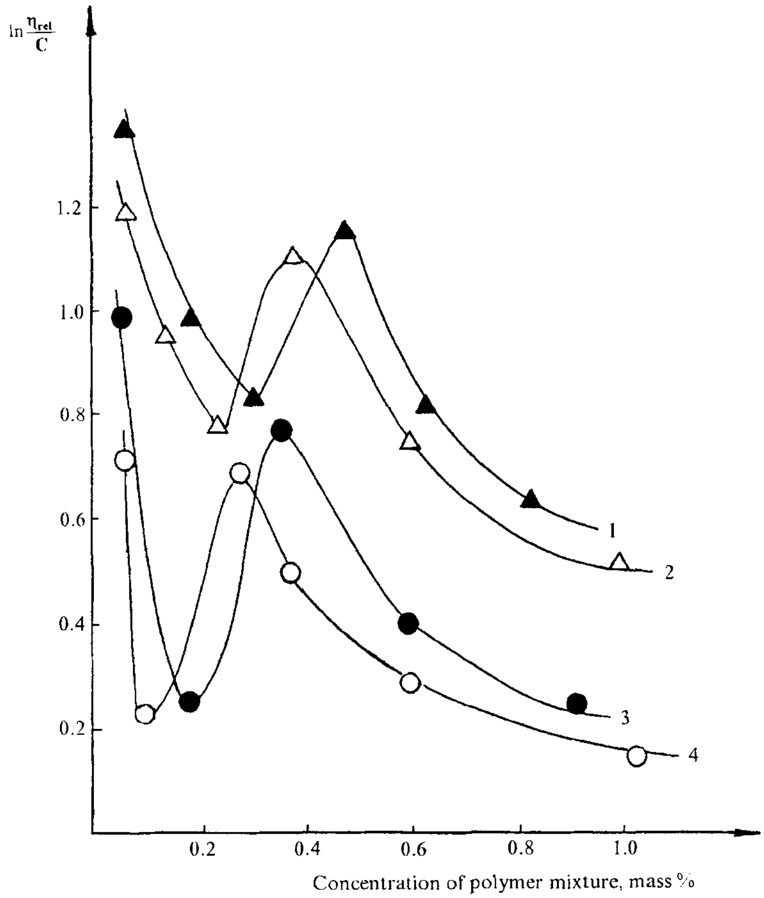

FIGURE 2 Dependency of the logarithm of reduced viscosity of solutions on the concentration of polymers in mixtures for the PVC-PMMA system: 90 : 10 mass % (1, 3); 50 : 50 mass % (2, 4) in CHN (1, 2) and TCP (3, 4) at 423 K.

monotonic change in TCP (Fig. 4) is the results of the interaction of two factors:

a) Because of the chemical influence of the second polymer the rate of PVC degradation increases in both solvents (influence of monomers);
b) Because of the change of structural-physical characteristics, namely the increase of the association degree of macromolecules caused by

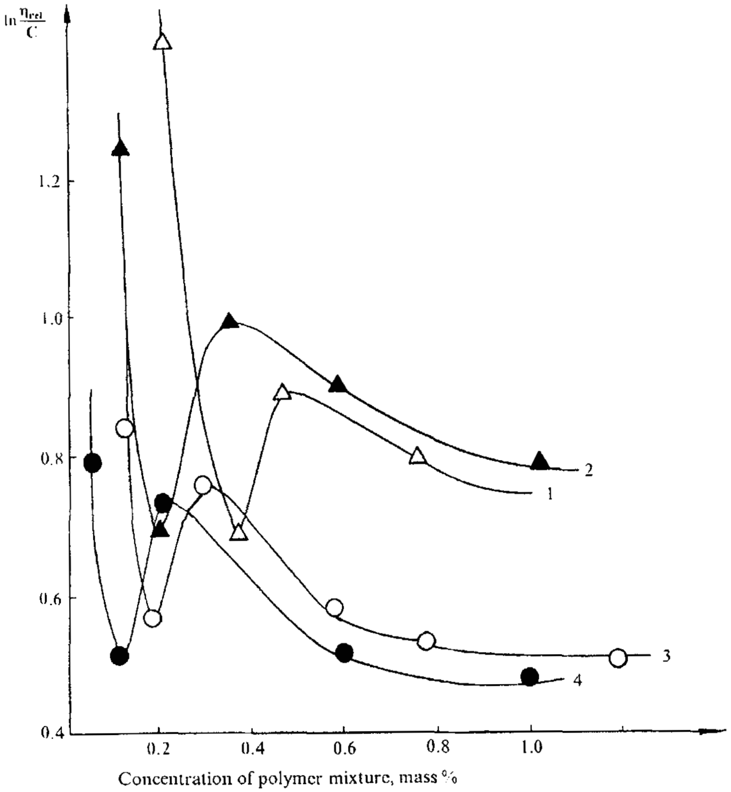

FIGURE 3 Dependency of the logarithm of reduced viscosity of solutions on the concentration of polymers in mixtures for the PVC-PS system: 90 : 10 mass % (1, 3); 50 : 50 mass % (2, 4) in CHN (1, 2) and TCP (3, 4) at 423 K.

adding the second polymer – the change of PVC degradation rate is different. In this case, it is provided by different solvation ability of solvents in relation to polymer.

Similar to the case of association of PVC macromolecules caused by simple concentration of the solution, adding of the second polymer (PMMA, PS) with low thermodynamic affinity to PVC induces a decrease of PVC degradation in CHN, and its increase in TCP. The rate of PVC dehydrochlorination has an extreme. It decreases as a result of aggregation of macromolecules and increases due to excretion of a monomer if the experiment is conducted in CHN.

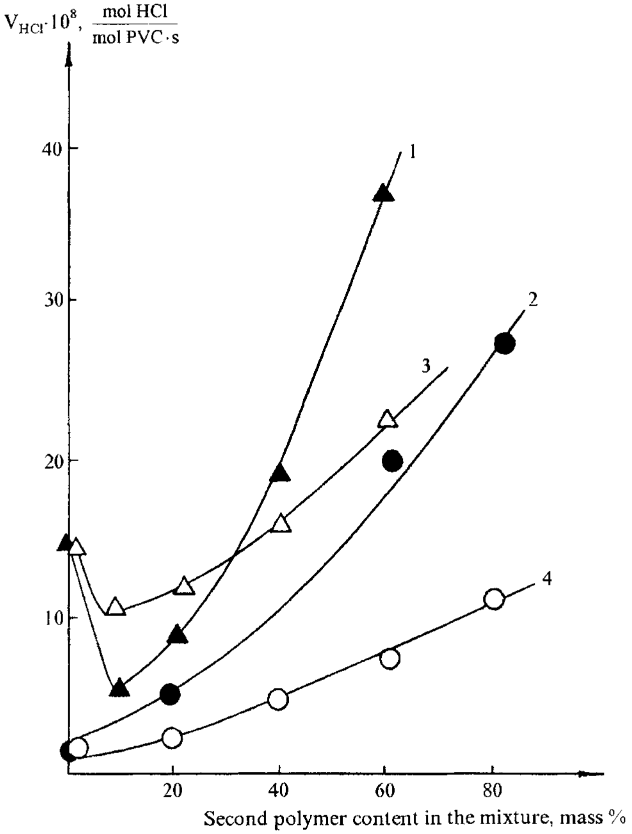

FIGURE 4 Dependency of the rate of PVC thermal dehydrochlorination in mixtures with PMMA (1, 2) and PS (3, 4) in CHN (1, 3) and TCP (2, 4) on the mixture composition at 423 K.

It is evident that solutions of polymer mixtures represent rather complicated systems at concentrations of several percents. These systems are composed of associated molecules and display specific chemical behavior. Polymer objects obtained by composition of polymers in melt are more complicated, because the properties and behavior of mixtures are defined not only by mutual compatibility and physicochemical affinity of two polymers, but also by the way of combination of the polymers.

At formation of samples under the conditions of melt flow, the structure of polymer objects is fixed at rapid cooling as a consequence of high viscosity of polymer melts and evidently remains at further heating of the samples in the absence of dynamic tensions, at least for the duration of experiments. This allows us to obtain a series of mixture composites with various microstructures from the melts. Viscosity anomalies at polymer flow were observed for tested PVC-PMMA and PVC-PS polymer pairs. Three cases are noted (Fig. 5).

1. A one-phase system; association degree of each component grows that leads to an increase of viscosity;

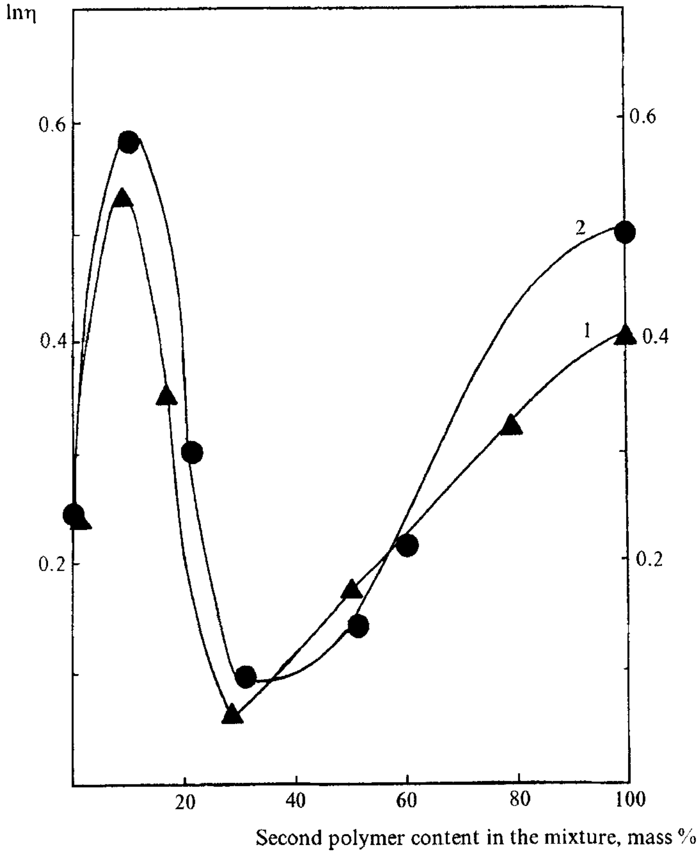

FIGURE 5 Dependency of the logarithm of melt viscosity on the composition of polymer mixture for PVC-PMMA (1) and PVC-PS (2) systems at 463 K, shift tension $\tau = 1.61$, and $PbSiO_4$ content of 3 mass parts.

2. The system transits into metastable state; a large amount of microemulsions is separated in the specific volume; viscosity decreases;
3. A two-phase system; the number of particles decrease due to their structuring; viscosity increases.

The minimum of viscosity logarithm, reached on flow curves, corresponds to the formation of the maximum number of microemulsion particles. Figure 5 shows that the position of the minimum point of $\lg\eta$ depends on the nature of polymers composing the mixture. Definite changes in the rate of PVC dehydrochlorination in mixture samples correspond to those in the viscous characteristics of PVC-PMMA and PVC-PS systems, which reflect changes in their structural-physical state. The change of PVC dehydrochlorination rate has an extreme depending on the second polymer content, the minimum of the degradation rate (Fig. 6, curves 1, 2) corresponding to the minimum of $\lg\eta$.

For mixtures of the same polymers obtained by mixing low-dispersed powders a different dependence of V_{HCl} on the mixture composition is observed. The rate of PVC dehydrochlorination decreases to a limit value and then remains constant with the increase of the second polymer content (Fig. 6, curves 3, 4). The inhibition of PVC degradation is bound to the influence of PMMA and PS depolymerization products under the conditions of PVC degradation in the absence of a solvent. In this connection the regularities observed are easily explained considering the change of the accesibility of polymer macromolecule chains for interaction with each other.

It is evident that at limited mutual solubility of selected polymer pairs, testified by the view of flow curves, chemical interaction of PVC macromolecules with the products of depolymerization of second polymers – methylmethacrylate and styrene – will be localized on the surface of the polymer contact that appears in the sphere (1) – one-phase system, and (2) formation of microemulsion. The efficiency of the influence, caused by the second polymer on PVC, increases for structures of types 1 and 2. This leads to more intensive decrease of the rate. At higher content of the second polymer, when the structure of polymer mixture formed corresponds to the type (3) – the two-phase system, the conditions of PVC macromolecule interaction with the

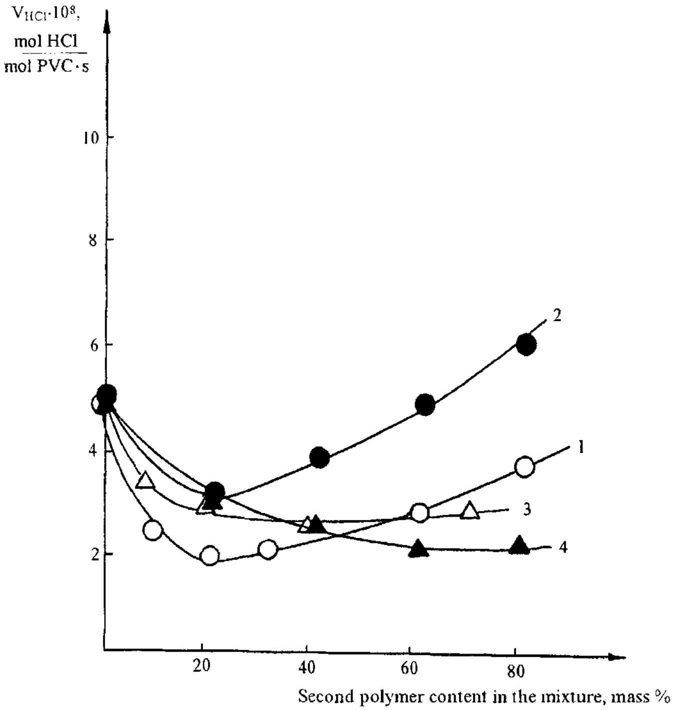

FIGURE 6 Dependency of thermal dehydrochlorination rate of PVC mixed with PMMA (1) and PS (2) for the mixtures obtained by combination in melt (1, 2) and associated co-precipitation (3, 4) in the presence of N_2 at 423 K.

products of PMMA and PS decomposition deteriorate due to deterioration of the polymer phase dispersion. As a consequence, the degree of PVC inhibition by the second polymer decreases, and the rate of PVC degradation tend to increase.

Thus, the structural-physical state of polymer mixtures, dependent on the way of the composite obtaining and affinity of polymers, generally defines chemical behavior of polymers, thermal stability of PVC, in particular. Forming polymer objects *via* changing structural-physical characteristics one may obtain composites with the same composition but characterized by essentially different rate of PVC dehydrochlorination.

Mixtures of polymers were prepared by co-precipitation from associated solution and combination in melt. Melts in polymer mixtures were prepared in viscosimeter MV-3M. To prevent degradation of polymers at combination of mixtures a stabilizer of PVC thermodegradation was added (lead silicate). The melt flow through capillary due to pressure difference between its ends, created by a weight, allows us to measure viscosities of melts of polymers and their mixtures. Solutions of polymer mixtures were prepared by mixing of solutions of pure polymers of equal concentration.

Solvents were purified by distillation. Study of viscosity of polymer solutions and their mixtures were performed according to standard technique with the help of Ubelode viscosimeter. Study of the rate of PVC dehydrochlorination was performed in a reactor according to technique, described in [6].

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