Texas Journal of Multidisciplinary Studies
https://zienjournals.com

ISSN NO: 2770-0003
Date of Publication: 11-03-2022

Investigation of the Influence of the Nature of the Solvent on the Properties of Solutions of Grafted Triacetate Copolymers

Karimova Zilola Makhmudovna
Assistant of the Department "Chemiya"
Bukhara Engineering and Technological Institute

Annotation: In our urbanized rapidly developing world, interest in an extensive class of organic polymers, and methods of grafting various vinyl monomers to them, has increased dramatically, which affects the physicochemical properties of the polymers themselves, and polymer materials, thus giving Cellulosic materials a number of valuable properties and expanding the scope of their application.

Keywords: Polymers, flexibility, the above, casting, granular product, developed, method, polymerization, dispersion of emulation, suspension, viscosity, molecular weight, initiator, emulsion, free radicals.

Most polymer mixtures are incompatible because they do not form a homogeneous homogeneous phase, this is due to the greater viscosity of polymeric fluids, which makes it difficult to achieve equilibrium, solutions. In polymer mixtures, macrodislation does not occur, even if the mixture is actually biphasic, the delamination in it is thermodynamically determined. This circumstance is very useful in applied terms, but it creates significant difficulties in determining the phase composition of mixtures and the need to study the properties of polymer mixtures in solution, where it is possible to establish the phase composition, and to investigate the structure of each phase separately and the mixture of polymers as a whole.

One of the important aspects in this direction is the solution of the problem of predicting the change in the rheological properties of polymers during mixing. The viscosity of the polymer mixture in some cases can be several times less than the viscosity of the original components, which is very important in connection with the problem of reducing the viscosity of concentrated polymer solutions.

As experience shows, the compatibility of the reacting components of the mixture has a significant impact on the quality of the products obtained. In this regard, for the successful management of the technological process, it is necessary to have information about the compatibility of the specific polymer materials used and the possibility of predicting the properties of the resulting reactions, mixtures. polymers[1,2].

The study of the compatibility of polymers and the rheological properties of polymer mixtures in a common solvent was carried out on the example of the study of the properties of a mixture of industrially important polymer products: (cellulose triacetate) and (poldi-2-methyl-5-vinylpyridine)[3-7].

The study of the properties of polymer mixtures in a general solvent is not only of applied importance, but is also important from the point of view of the theory of compatibility, the development of which is currently one of the most important physicochemical tasks of the modern doctrine of polymers.

The purpose of this work is to study the influence of the structure and nature of the solvent on the properties of grafted copolymers of cellulose triacetate with poly 2-m 5-vinylpyridine using for this purpose the study of mixtures obtained as a result of the reaction optical, sorption and viscosometric methods.

The papers show that the polymer-polymer-solvent system is more complex than the mixture system of two polymer-solvent liquids. The principle of additivity without a corresponding theoretical justification cannot be applied here. The development of research in this area has been folded in such a way that, first of all, the systems cannot be applied here. and the polymer-polymer-solvent was studied by methods of physicochemical analysis.

Among the properties studied depending on the composition was viscosity[4,5]. Viscosity is one of the most studied and defined properties of polymer solutions, allowing us to conclude not only about the behavior of the macromolecule itself, but also about the interaction between the components of the system. When measuring the viscosity of polymer mixtures in a common solvent, it was found that it usually does not obey the rule This deviation has been chosen by many authors to assess the compatibility of the polymers being mixed. It is believed that the reason for the deviation of viscosity from the additivity rule is the formation of vassociates not only homogeneous polymers or heterogeneous ones. The crooked "viscosity-composition" must be associated with the curve obtained as a result of theoretical or experimental calculations , for the same components in the case of their ideal mixing. Then the magnitude and nature of the deviation between the two curves can be judged on the interaction of the components, even Arrhenius proposed an empirical formula for determining bindness of mixtures of binary liquids.

$Ln\eta = N_{1}ln\eta_{1} + N2ln\eta2$(1)

wherein N1 and N2 are the molar lobes of the components,
η_1 and η_2 are the corresponding viscosity values.

This formula, although approximate, shows that the viscosity changes non-additively with a change in the composition of the components. For a mixture of polymers in solution, the equation coincides with the experiment only in the field of small concentrations of reactants The viscosity characteristic for solutions of polymer mixtures is described by the formula .

$[h] = [h]_{1x1} + [h]2x2$(2)

GDe x1 is the volume or weight fraction of component 1.

For dilute solutions of polymer mixtures, an equation was proposed where the specific tenderness of the solution of the mixture is theoretically sold η ud.cm.

$$\eta_{\text{уд.см}} = [\eta]_1 c_1 + [\eta]_2 c_1 + b_{11}c_1^2 + b_{22}c_2^2 + 2\sqrt{b_1 b_2}c_1 c_2 \quad (3)$$

Where $b_{12} = \sqrt{b_1 b_2}$; b11, b_{22} - interaction parameters between heterogeneous polymer molecules.

To distinguish between the experimental and theoretical values of the theor parameter $\Delta и_{12} = b_{12}\text{эксп} - b_{12}$in solution, an equation is used. for the ideal viscosity of polymer mixtures in c $b = \frac{b_{11} + b_{22}}{2}$ and in c$b = X[\eta]^2$,

The authors believe that the equation given in this work gives a more accurate coincidence with the experimental data.

In the paper, the viscosity values obtained experimentally for solutions of mixtures of polystyrene and PIB-na in toluene were compared with the calculated values according to the equation:

$$\eta_{\text{уд.}} = \lambda\omega_1^2 + N\omega_1 + P;\ \eta = (\omega_1\eta^{\frac{1}{2}} + \omega_1\eta_2^{\frac{1}{k}})^2 \quad (4)$$

where, ω_1 is the weight fraction of one of the components, λ,M,P are coefficients depending on the molecular weight, concentration and constant of Haggipsak; η_1 andη_2 is the viscosity of the components, α is the exponent of the equation [η] = KM $^{\alpha}$. The first of these equations is applicable in a limited area of concentrations, the second can be applied to any concentration[2,4,7].

For the triple system as polymer A, polymer B, the solvent obtained a formula for determining the viscosity of the mixture:

$$\eta_{ij} = \frac{\eta_i}{\Pi_{ij}(1-2{,}5\vartheta_1+11\vartheta_i^5+11{,}5\vartheta_i^7} \quad (5)$$

The equation has been tested on a number of systems. For the PMMA-PS pair in m-xylene, viscosities at different concentrations were calculated and then extrapolated to zero concentration. At the same time, the characteristic experimental dependence of viscosity on the composition of the mixture is well consistent with the calculated one.

In the field of studying homogeneous mixing of polymer mixtures, an analytical expression was obtained linking the viscosity of polymer solutions with the concentration and other characteristics of the reaction components:

$$\eta_{\text{см}} = \eta_o \text{P}(1 + \text{c}_i[\eta]_i < \gamma_i >)^{x_i/<\gamma_i>} \quad (6)$$

where η_o is the viscosity of the solvent, P is the product of the co-primers, c_i is the concentration of the i-th component, and the $\text{C} = \sum \text{c}_i$ value $x_i = \frac{c}{c}$ is determined by:$< \gamma_i >$

$$< \gamma_i > = \frac{1}{[\eta]_i}\sum \gamma_{ij} x_i [\eta]_j \quad (7)$$

J_{ij} is a coefficient that characterizes the interaction of the i and j-th components; the sum sign means that all components are summed up by .

Thus, accounting for intermolecular, hydrodynamic and dynamic interactions gives a relatively simple ratio for viscosity. In the field of small concentrations, the equation becomes as follows:

$$\frac{\eta_{\text{см}}}{\eta_o} = 1 + \mathrm{C}[\eta] + \frac{1}{2}c^2 \sum x_i x_j [\eta]_i [\eta]_j \left[\gamma_1 + k_j + \frac{\gamma_{ij}+\gamma_{ji}-2\gamma_{ij}}{2}\right] + \cdots \quad (8)$$

where kj is the Häggins constant for the solution of the j-th component.

The paper gives a ratio between the viscosity of the polymer mixture itself and the viscosities of the initial samples of polymers of the same concentration.

$$\eta_{\text{см}} = \eta_1^{x_1(1+x_1\delta_1)} \eta_2^{x_2(1+x_2\delta_2)} \{1 - c x_1 x_2([\eta]_1\delta_1 + [\eta]_2\delta_2)\} \quad (9)$$

Where η $_1$ and η $_2$ are the viscosities of solutions of concentration C for pure components. The value of δ $_1$ and δ $_2$ is equal:

$$\delta_1 = \frac{\gamma_{11}[\eta]_1 - \gamma_{12}[\eta]_2}{x_1\gamma_{11}[\eta]_1 - x_2\gamma_{12}[\eta]_2}; \quad ; \quad (10)\ \delta_2 = \frac{\gamma_{22}[\eta]_2 - \gamma_{12}[\eta]_1}{x_2\gamma_{22}[\eta]_2 - x_1\gamma_{12}[\eta]_1}$$

The paper [20] also considers the change in the characteristic viscosity of polymers in a liquid that is a solution of another polymer:

$$[\eta]_{12} = \frac{[\eta]_i}{1 + \gamma_{12}\ c_2[\eta]_2} \quad (11)$$

The ratio allows you to determine the coefficient of mutual compression. A similar analysis is used in the work[2,6].

It was obtained for a mixture of PS and PMMA in toluene a value for γ $_{12}$ = 0.33, for a mixture of polyvinylpyrrolidone with PMMA in dichloroethane, using the ratio, the authors obtained a value of γ $_{12}$ = 0.45.

These ratios are valid in the region of a single-phase solution. During the transition of the system to a metastable or unstable state , heterophase fluctuations occur, which are the embryos of new phases. At the same time, part of the polymer is in the form of droplets of the emulsion, but to calculate the viscosity of such a system, data on the number of polymers that have passed into the new phase are needed.

The objects of the study were polyure-trailer cellulose triacetate (TSPC) 59.2%, bound by acetic acid, and MM $_\eta$ = 7.4 * 104 and flexible chain poly-2-methyl-5-vinylpyridine (PMDP) synthesized by radical polymerization in the presence of dinitryl-azobis-iso butyric acid at 60 ° C. Fractionation of VMVP was carried out by fractional precipitation from 2% solutions in the chloroform sulfur ether system. Molecular weight (MM) of PMIP fractions was determined viscosimetric data (Table 1).

Table 1.

VHWP	Solvent	[η] dl/d	To	A	$\overline{M}_r \cdot 10^{-5}$
1	Methyl-ethylketone	0,65	1,9*10-4	0,64	3,3
2		0,43			1,9
3		0,25			0,74

Synthesis of grafted cellulose copolymers with poly-2-methyl-5-vinylpyridine.

Currently, in polymer chemistry, there is great interest in methods that make it possible to carry out controlled synthesis of graft copolymers, controlling the degree of penetration, molecular weight and number of grafted chains. In this regard, graft molymerization in the presence of trivalent cobalt salts is of particular interest. allows you to adjust these parameters. To this end, we synthesized grafted cellulose copolymers with PMIP of various compositions and structures [5,7,10].

Cotton cellulose purified according to the standard method was used as starting materials. The MVP was ordered immediately after fractional distillation under vacuum. The reaction was also carried out at proportions close to those described earlier; in an aqueous medium, with a content in the reaction mixture of 0.25 mol / l of free sulfuric acid, in nitrogen current, with intensive mixing. At a constant concentration of the nomer of 0.612 mol / L and a temperature of 0 ° C With the concentration of the catalyst varied in the range of 0.05-2.0 mmol, L. The resulting homopolymer was removed by extraction of 0.02 N with a solution of sulfuric acid. Control of the reaction was carried out by the output of the graft copolymer and the coeffient of polymmerization (CP) of the grafted chains, which were released by hydrolysis of the cellulosic part of the copolymer 72 wt% sulfuric acid. KP of the grafted chains was determined by the characteristic viscosity of the polymer isolated after hydrolysis of the cellulosic part of the copolymer in dimethylformamidem . The resulting copolymers of C-PMDP are insoluble in organic solvents and cadoxene. By esterifying the cellulosic part of the copolymer with glacial acetic acid with trifluoroacetic acid anhydride, TSPC-VMVP copolymers soluble in organic solvents were obtained.

The content of VMVP in the copolymer was determined by UV spectroscopy for the absorption of light by solutions of copolymers in methylene chloride at $\lambda = 270$ nm[2-7] by the method of light scattering of solutions, the molecular weights of the graft copolymers were determined. The Kazhav method investigated moderately concentrated solutions of TSPC + PMDP mixtures in polymer solvents. The coefficient of intermolecular thermodynamic interaction - γ_{12} - was determined.

The thermodynamic stability of graft copolymers and polymer mixtures was studied and the average free mixing energies of polymers - Δ gx - were calculated.

Complexes of PTC-UMVP-nickel primolymers were obtained and the effect of MM side chains on the reduced viscosity of complexes in solution was studied.

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