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Radical Polymerization of Vinyl Acetate in Individual and Mixed Solvents

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Abstract—The kinetics of polymerization of vinyl acetate in individual and mixed solvents was studied. The reaction rate constant and the rate of chain transfer in the mixed solvent were calculated, molecular weights and some adhesive characteristics of poly(vinyl acetate) obtained by the radical polymerization in solution were determined. A comparative analysis of the polymers obtained in the individual and mixed solvents was performed. It is shown that the change in the solvent composition can affect the rate of reaction and the poly(vinyl acetate) adhesive properties.

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Solvents used in the polymerization of vinyl acetate affect significantly the molecular weight and properties of the resulting polymer [1]. The polymerization of vinyl acetate was studied in methanol [2], methyl acetate, and mixtures thereof [3] with water, as well as in the ethanol medium [4]. The influence of water on the vinyl acetate polymerization in various environments was separately examined. For example, in [5, 6] the influence of water was described on the polymerization rate and macromolecular parameters of the polymer. Egoyan explains the accelerating effect of water by the deterioration of thermodynamic quality of solvent, which leads to conformational changes in the polymer. Therefore, by changing the thermodynamic quality of solvents or using the solvent mixtures it is possible to adjust the kinetic and molecular parameters of the polymer.

The aim of our work was to study the effect of a mixture of organic solvents on the kinetic parameters of polymerization and the properties of poly(vinyl acetate).

To compare the effect of solvent mixtures on the polymerization of vinyl acetate it was necessary initially to assess the impact of individual solvents on this process.

Table 1 shows the rates and the rate constants of the polymerization, the yield and molecular weight of the poly(vinyl acetate) samples obtained in ethyl acetate, ethanol, and *t*-butanol. The highest rate and rate constants of the reaction were observed in ethyl acetate and *t*-butanol, and the lowest, at the polymerization in ethyl alcohol (Table 1). This can be associated with the chain transfer on the solvent. The chain transfer should not affect the rate of the monomer polymerization, but usually it decreases, since at the interaction of the growing chain with the solvent less reactive radicals are formed which often leads to the chain termination. This phenomenon occurs perhaps at the polymerization of vinyl acetate in ethyl alcohol. On the contrary, a high rate of the polymer formation in ethyl acetate is due to the fact that the radicals $^{\bullet}CH_2COOC_2H_5$ (**I**) are similar to vinyl acetate radicals by reactivity and polarity [7]. The high rate of polymerization observed in the synthesis of poly(vinyl acetate) in the presence of *t*-butanol may be due to the low activity of the hydrogen atom of the hydroxy group at the tertiary carbon atom, as evidenced by the value of the coefficient of chain transfer to solvent (K_s in Table. 2) [8].

The greatest value of the chain transfer coefficient corresponded to ethyl alcohol, where the poly(vinyl acetate) was obtained with M = 11 600, while in *t*-butanol, which had $K_s = 0.58\times10^{-4}$, the poly(vinyl acetate) formed had M = 379 000.

The low value of K_s in the polymerization of vinyl acetate in *t*-butanol leads to the fact that the fast-growing macromolecules increase the viscosity of the reaction system. The polyvinyl acetate solution in

Table 1. Initial rate of polymerization and the rate constants (*k*) of vinyl acetate polymerization in various solvents at 68ºC, the yield and molecular weight of poly(vinyl acetate)

Solvent	$\upsilon \times 10^3$, mol l^{-1} s^{-1}	$k \times 10^3$, s^{-1}	Yield, %[a]	M[a]
Ethyl acetate	2.17	0.54	74.2	61400
Ethyl alcohol	1.14	0.24	58.3	11600
tert-Butyl alcohol	2.15	0.53	67.0	379000

[a] The synthesis duration 90 min.

Table 2. Effect of the reaction mixture composition at the vinyl acetate polymerization on the initial reaction rate and the polymerization rate constant, the coefficient of chain transfer to solvent and the molecular weight *M* of polyvinyl acetate

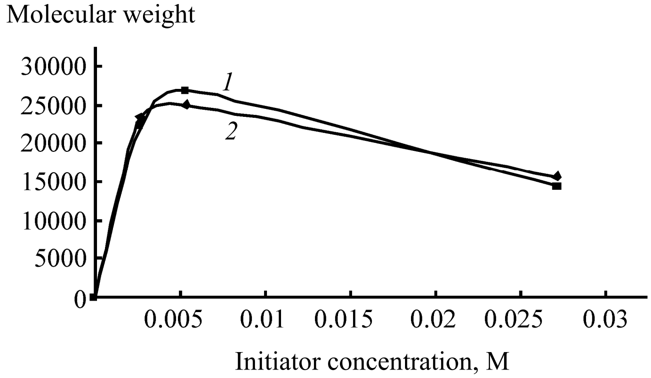
Solvent content in the reaction medium, vol %			$\upsilon \times 10^3$, mol l^{-1} s^{-1}	$k \times 10^3$, s^{-1}	$K_s \times 10^4$	M	Yield, %
EtOH	EtOAc	*t*-BuOH					
50	–	–	1.14	0.24	26.00	11600	58.3
37.5	12.5	–	1.08	0.23	26.55	18600	40.3
25.0	25.0	–	0.71	0.14	26.38	25000	37.0
12.5	37.5	–	0.74	0.15	17.53	36750	32.2
–	50.0	–	2.17	0.54	2.75	61400	74.2
37.5	–	12.5	0.91	0.19	32.88	17200	38.9
25.0	–	25.0	0.99	0.20	24.93	26900	27.3
12.5	–	37.5	1.08	0.23	11.83	49100	45.6
–	–	50.0	2.15	0.53	0.58	379000	67.0
–	37.5	12.5	0.62	0.12	2.50	76450	48.2
–	25.0	25.0	0.94	0.20	3.37	88500	32.5
–	12.5	37.5	1.95	0.45	2.93	125000	52.4

t-butanol has thickened after 45 min, while in ethyl alcohol even in the reaction performed for 90 min the solution remained not viscous. With the accumulation of the polymer in the system the reaction rate of intermolecular chain transfer involving both the primary radicals and macroradicals increases, which leads to the formation of branches at the acetate groups and the main chain of polyvinyl acetate. Therefore, polyvinyl acetate obtained in *t*-butanol has a higher *M* value compared with that obatained at the use of ethyl acetate or ethyl alcohol.

Assessing the impact of initiator concentration on the polymer molecular weight using a mixture of solvents shows that the optimal concentration of azoisobutironitrile is 0.0054 M, the same as with the individual solvents (see the figure).

Table 2 shows the kinetic parameters of polymerization of vinyl acetate in mixed solvents. By the nature of the kinetic curves it can be concluded that the rate of polymerization of vinyl acetate and the polymer yield in the individual solvents is higher than in mixtures. The polymerization of vinyl acetate in a mixture of any pair of solvents is characterized by a lower value of the rate constant of polymerization compared to polymerization in the individual solvents. The coefficient of chain transfer to solvent mixture is significantly higher than in the systems with a single solvent. The explanation for this probably lies in the formation of a mixed solvation shell of solvents, which results in appearance of a more active particle capable of reacting with the radical of the macromolecule faster compared with the radicals formed by individual solvents. Therewith the formed radicals are less active than the primary ones resulting in slower polymerization, as is observed at a low degree of conversion (Table 2).

After accumulation of such radicals in the system to a certain critical concentration, the polymerization rate



Dependence of the effect of initiator concentration on the molecular weight of poly(vinyl acetate) obtained in the solvent mixtures: (*1*) *tert*-butyl alcohol–ethanol, (*2*) ethyl acetate–ethanol.

increases, but it does not allow the achievement of the polymer yield corresponding to that of poly(vinyl acetate) (in a fixed period of time 90 min) obtained in individual solvents (Table 2).

The use of solvent mixtures allows varying the polyvinyl acetate M value in the range of 17000 to 89000. At the same time it was impossible to obtain a polymer with a high M characteristic of polyvinyl acetate obtained in *t*-butanol.

Table 3. Estimated influence of the solvent nature and concentration on the tensile strength (toward steel) and shear strenght (toward wood) of the polyvinyl acetate

Solvent content in the reaction medium, vol %			Tensile strength, MPa	Shear strength, MPa
EtOH	EtOAc	*t*-BuOH		
50	–	–	0.15	0.26
37.5	12.5	–	0.31	3.36
25.0	25.0	–	0.33	2.98
12.5	37.5	–	0.86	2.42
–	50.0	–	0.54	0.16
37.5	–	12.5	0.59	1.08
25.0	–	25.0	0.75	2.60
12.5	–	37.5	0.05	0.27
–	–	50.0	0.23	0.11
–	37.5	12.5	0.18	1.05
–	25.0	25.0	0.24	1.24
–	12.5	37.5	0.07	1.56

As is known, in the radical polymerization in different solvents the phenomenon of chain transfer occurs not only on the monomer, but also on the solvent. This results in the formation of the radicals including a fragment of both the solvent and the monomer, which in turn may initiate a new polymer chain or may enter into a recombination or disproportionation, changing the structure of the polymer. As a result, graft polymers are formed. Thus, the introduction during the polymerization of the solvent molecules to the polymer macromolecule in a specific ratio can lead to a modification of the expected polymer chain and as a consequence to a change in the physical and mechanical properties of the polymer.

Since the polyvinyl acetate obtained by the solvent method is widely used as adhesive, it must possess high adhesion characteristics. Therefore, it is expedient to study the effect of solvents on the adhesive characteristics of obtained polymers (Table 3).

The samples on the basis of individual solvents by their adhesive properties are inferior to almost all adhesives synthesized in solvent mixtures. The best properties have the polyvinyl acetate samples using a solvent mixture of ethanol and ethyl acetate with M = 18000–37000.

EXPERIMENTAL

The solvents used were ethyl acetate, ethyl alcohol, *tert*-butyl alcohol (*t*-butanol), and mixtures thereof. All used solvents were purified by the known techniques [9, 10].

We used vinyl acetate of AC brand (TU 6-11-0209955-1-88, the highest grade), as the initiator was used azobisisobutyronitrile (porophore-57).

The polyvinyl acetate synthesis was carried out in a three-neck flask equipped with a reflux condenser, using different solvents. The flask was charged with a mixture of monomer and a solvent (a combined solvent) in the calculated ratio and was heated on a water bath to a temperature of 67–69°C with vigorous stirring. Then the calculated amount of initiator (0.1 mol %) was added to the reaction mixture. The reaction was carried out for 90 min after adding the initiator. The kinetics was studied by the analysis of the aliquot samples taken from the reaction mixture.

Purification of polymers from the unreacted monomer was carried out by reprecipitation with water from the solution in a mixed solvent.

The viscosity-average molecular weight of the polymer was determined in benzene at 30°C using an Ubbelohde viscometer with the capillary of 0.73 mm diameter. The concentration of polymer was 2.5 wt %. The M value was calculated with the Mark–Kuhn–Houwink equation ($K = 5.63\times10^5$ dl g^{-1}, $\alpha = 0.62$) [11].

The polymer yield was determined by gravimetric analysis, the determined substance was precipitated from the solution as a poorly soluble compound [12].

The calculation of the kinetic parameters of the reaction was performed by the integration method. The reaction order corresponded to the first order [13]. The coefficient of chain transfer to solvent was determined by the Mayo equation [14]:

$$1/\bar{p} = 1/\bar{p}_0 + C_s([S]/[M]),$$

where C_s is the coefficient of chain transfer to solvent, [S] is the solvent concentration, [M] is the monomer concentration, $\bar{p}$ and $\bar{p}_0$ are the average polymerization degrees in the presence and in the absence of the solvent, respectively. The coefficient of chain transfer to solvent was found from the slope of the straight line dependence of $1/\bar{p}$ vs. [S]/[M].

Shear strength was determined according to GOST 14759-69 on a tensile testing machine Inspekt mini 3kN at the rate 50 mm min^{-1}. The ultimate tensile strength was measured in accordance with GOST 14760-69 on the tensile testing machine RMI-250 "Metallist" at the rate 50 mm min^{-1}.

REFERENCES

1. Ushakov, C.N., *Polivinilovyi spirt i ego proizvodnye* (Plyvinyl Alcohol and Its Derivatives), Leningrad: Akad. Nauk SSSR, 1960, vol. 1, p. 144.
2. Aleksandru, L., *Vysokomol. Soed.*, 1961, vol. 3, no. 2, p. 306.
3. Nikolaev, A.F., *Plast. Massy*, 1969, no. 4, p. 11.
4. Sorokin, A.Ya., *Plast. Massy*, 1970, no. 11, p. 11.
5. Egoyan, R.V., *Vysokomol. Soed., (B),* 1988, vol. 30, no. 1, p. 8.
6. Egoyan, R.V., *Vysokomol. Soed., (B),* 2001, vol. 43, no. 2, p. 362.
7. Nikolaev, A.F., *Sinteticheskie polimery i plasticheskie massy na ikh osnove* (Synthetic Polymers and Plastics Based on Them), Leningrad: Khimiya, 1966, p. 768.
8. Rozenberg, M.E., *Polimery na osnove vinilatsetata* (Polymers Based on Vinyl Acetate), Leningrad: Khimiya, 1983.
9. Avvakumova, N.I., *Laboratornye raboty po tekhnologii plasticheskikh mass* (Laboratory Works on the Plastics Technology), Kazan, 1991.
10. Artimenko, A.I., *Spravochnoe rukovodstvo po khimii* (Chemistry Guide. Handbook), Moscow: Vysshaya Shkola, 2003.
11. Avvakumova, N.I., *Praktikum po khimii i fizike polimerov* (Practicum on the Chemistry and Physics of Polymers), Moscow: Khimiya, 1990.
12. Vasil'ev, V.P., *Analiticheskaya khimiya. Gravimetricheskii i titrimetricheskii metody analiza* (Analytical Chemistry. Gravimetric and Iitrimetric Methods of Analysis), Moscow: Vysshaya Shkola, 1989.
13. Berlin, A.A., *Kinetika polimerizatsionnykh protsessov* (Kinetics of the Polymerization Processes), Moscow: Khimiya, 1978.
14. Kochnev, A.M., *Khimiya vysokomolekulyarnykh soedinenii* (Chemistry of Highmolecular Compounds), Kazan: Technol. Univ., 2009.