

SYNTHESIS OF POLYACRYL THICKENERS BY RADICAL PRECIPITATION POLYMERIZATION

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Lightly cross-linked polymer thickeners on the basis of acrylic and methacrylic acid have been synthesized with the use of radical precipitation polymerization. The influence of introducing hydrophobic units, cross-linking degree, the nature of neutralizing agents, neutralization degree of acidic units, and other factors upon thickening properties of obtained polymers in water, as well as water mixtures with glycerol or propylene glycol, has been determined.

Keywords: acrylic acid, methacrylic acid, alkyl (meth)acrylates, radical polymerization, lightly cross-linked polymers, thickeners, water, glycerol, glycols.

Introduction

Polyacrylic thickeners, obtained on the basis of acrylic acid (AA) and methacrylic acid (MAA) are widely used as modifiers of rheological properties for aqueous systems in textile industry [1], as well as for water-glycol de-icing fluids (DIF) of type IV, which are designed for preflight treatment of aircrafts in winter conditions [2]. In accordance with the conditions of use, such thickeners should achieve the necessary thickening degree of solutions at their minimal content in mixtures, also they should exhibit the optimal change of viscosity at various tensions and temperatures. This is accomplished by varying the composition of polymers and their molar mass, by choosing the neutralizing agent, changing the neutralization degree of acidic units and other factors [3]. At present the lightly cross-linked hydrophobically modified polymers of AA and MAA, containing the units of higher alkyl acrylates or alkyl methacrylates, are the most widely used thickeners of acryl type. Interaction of hydrophobic alkyl fragments of such macromolecules in aqueous solutions enhances their thickening property [4, 5]. At that the degree of cross-linking, the molar mass of the polymer and the content of hydrophobic units should ensure retention of the polymer solubility in the used systems at all operating conditions. Quite often the hydrophobically modified polyacryl thickeners are synthesized with the use of radical precipitation polymerization in the medium of hydrophobic organic solvents [6, 7]. By way of trial-and-error selection of the solvent and the synthesis conditions it is possible to achieve precipitation of the polymers exhibiting the necessary set of properties in water and water-glycol solutions.

The aim of the present study is the synthesis by precipitations polymerization of thickeners on the basis of AA and MAA, differing in composition, cross-linking degree, the nature of neutralizing agents, and neutralization degree of acidic units, as well as evaluation of thickening properties of obtained polymers in aqueous solutions and in the systems water – propylene glycol (PG) and water – glycerol.

Experimental

Reagents that were used in the study: AA, n-butyl acrylate (BA) by "SIBUR-neftekhim", MAA, lauryl methacrylate (LMA), acrylamide (AAM), triethylene glycol dimethacrylate (TGM-3), and ethylene glycol dimethacrylate (DMEG) by "Aldrich".

Copolymerization of MAA and BA was carried out in cyclohexane, heptane, or benzene at various monomer ratios and their total concentration ($\Sigma[M]_0$) equaling 12 % m/m, in the presence of lauroyl pe-

roxide (1.0% mol of $\Sigma[M]_0$) as the initiator and DMEG (0.6 % mol of $\Sigma[M]_0$) as the cross-linking agent, at boiling temperature of the reaction mixture. The time of synthesis equaled 3 h. Homopolymerization of AA or its copolymerization with LMA (mole ratio 99.5 : 0.5), AAm or BA (mole ratio 95.0 : 5.0) was carried out at the total monomer concentration 13 % m/m in ethyl acetate medium, in the presence of 2,2'-azobis-(2,4-dimethylvaleronitrile) (0.1–0.2 % mol of $\Sigma[M]_0$) as the initiator and TGM or DMEG (0.2–0.5% mol of $\Sigma[M]_0$) as the cross-linking agent, at temperature 70 °C and synthesis time 2 h. After the synthesis the precipitated polymers were filtered and dried at reduced pressure and temperature 50–60 °C to constant mass. Then the weighed samples of the polymers were dissolved at intensive stirring in the aqueous solution of the neutralizing agent (in order to reach the predetermined neutralization degree of acidic units) or in the mixtures glycerol – water (60 : 40 % m/m), propylene glycol (PG) – water (50 : 50 % m/m), followed by neutralization with the concentrated aqueous solution of sodium hydroxide to pH 7-8.

Kinematic viscosity of the solutions of copolymers MAA–BA in DMFA (0.25 % m/m) and neutralized copolymers MAA–BA in aqueous solutions (0.2 % m/m) was determined, respectively, in viscosimeter VPZh-1 with capillar diameter 2.10 mm, and VPZh-2 with capillar diameter 0.73 mm at temperature 20 °C. Relative viscosity (η_{rel}) was determined according to the formula:

$$\eta_{rel} = \tau_p / \tau_x,$$

where τ_p and τ_x are flow times of solutions with a thickener and without a thickener, respectively, s.

Dynamic viscosity of the solutions of (co)polymers AA in the mixtures water – glycol and water – glycerol was measured in the apparatus Brookfield DV-II+Pro, furnished with the small-sample adapter and spindle #31 in Brookfield classification, at temperature 20 °C and various rotation speeds of the spindle.

Results and Discussion

Thickeners on the basis of hydrophobically modified polymethacrylic acid are mostly used for aqueous systems, therefore the synthesized copolymers MAA–BA have been tested in aqueous solutions. To choose the conditions of the synthesis, comparative experiments have been carried out in three nonpolar hydrocarbon solvents: heptane, cyclohexane, and benzene. The listed solvents are close to each other in polarity, that is, the solubility of the formed copolymers in them should differ insignificantly. However, the chain transfer constants C_s for these solvents differ, they equal $1.7 \cdot 10^{-4}$ for heptane, $0.1 \cdot 10^{-4}$ for cyclohexane, $0.075 \cdot 10^{-4}$ for benzene. Viscosity values of 0.2 % copolymer solutions in DMFA equal 1.5, 1.8, and 2.0 for the polymers obtained in heptane, cyclohexane, and benzene, respectively, at the same amounts of the monomer, the cross-linking agent, and the initiator. Thus, it has been shown that the molar mass of macromolecules increases with decrease of C_s value, exactly as expected. In the course of experimental study it has been also shown that the use of benzene as the medium for the reaction leads to decrease of the polymer yield. In addition, benzene is more toxic than heptane and cyclohexane. Therefore, cyclohexane has been chosen for further experiments. One of the key parameters, that influence the efficiency of the thickening polyacryl polymers, is the ratio of hydrophilic acidic units and the hydrophobic units of alkyl (meth)acrylates. The optimal value of this ratio depends on the nature of hydrophilic and hydrophobic units in copolymers, it should be selected individually for each system under investigation.

To choose the optimal ratio in the case of thickening aqueous solutions with MAA–BA copolymers the series of syntheses in cyclohexane medium has been carried out at various initial ratios of the acidic monomer and the esteric one, at

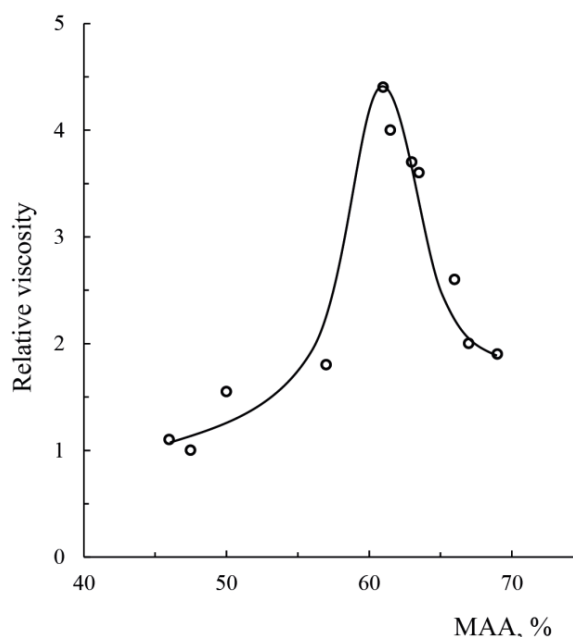


Fig. 1. Relative viscosity of the solutions of MAA–BA copolymers in DMFA as the function of the acidic unit content in them

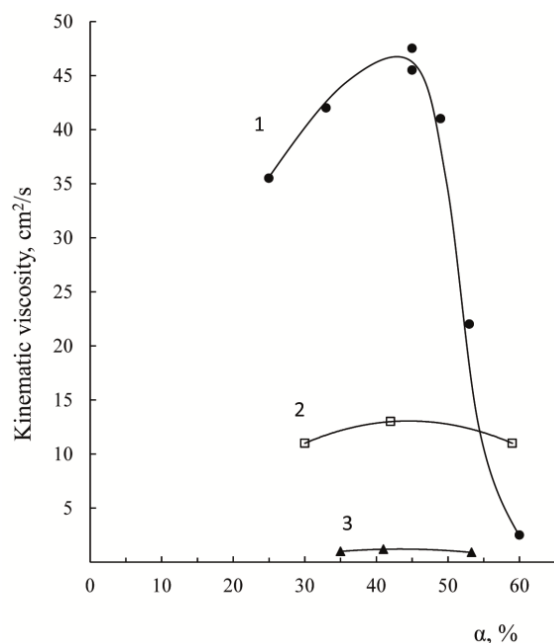


Fig. 2. Kinematic viscosity of the MAA–BA copolymers as the function of the acidic unit content and the degree of neutralization (α) by diethylamine. MAA : BA = 63:37 (1); 80:20 (2); 90:10 (3)

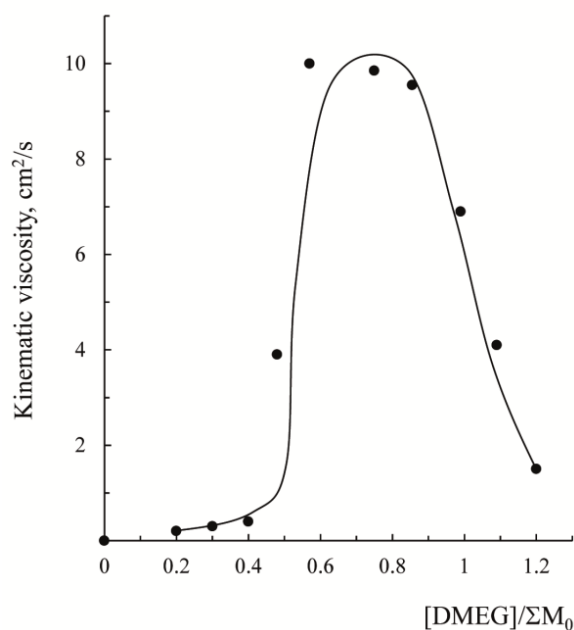


Fig. 3. Kinematic viscosity of the aqueous solutions of MAA–BA copolymers as the function of DMEG content in the initial monomer mixture

constant content of the cross-linking agent, namely, DMEG (0.6 % mol of $\Sigma[M]_0$). The obtained samples of the copolymers differ in the acidic unit content, which varies from 45 to 70 %. Figure 1 shows the influence of the acidic unit content on the viscosity of 0.2 % polymer solutions in DMFA. The maximal viscosity value, corresponding to the acidic unit content 62–64 %, is observed on the resultant curve. The relationship between the thickening property of polymers and the degree of acidic unit neutralization, represented in Fig. 2, supports the greater thickening property of copolymers containing 63 % MAA units.

Because of this, in the following experiments with the MAA–BA copolymer the influence of other factors has been evaluated at the ratio of monomer units 63:37.

An important factor, which influences the viscosity characteristics of the polymers, is the cross-linking degree that depends on content of the introduced cross-linking agent. Due to experimental study of DMEG content variation in the monomer mixture (Fig. 3) it has been established that the relationship between the thickening property of the MAA–BA copolymer and the initial DMEG content exhibits a clearly defined maximum.

Special consideration must be given to the steep rise of the thickening property at increasing DMEG concentration from 0.4 to 0.5 % mol. of the total concentration of main monomers ($\Sigma[M]_0$), as well as the steep decline of this property after increasing DMEG concentration from 0.9 to 1.0–1.2 % mol of $\Sigma[M]_0$. Observational data point at the interval of the optimal cross-linking degree for macromolecules, in order to achieve the greatest viscosity of their solutions (that is, the formation of macromolecular coils occupying the greatest volume in a solution).

The neutralization degree of acidic groups and the nature of neutralizing agent have a dramatic effect on the viscosity of aqueous solutions. Fig. 4 shows the kinematic viscosity values depending on the neutralization degree of acidic groups and the kind of the base used to neutralize the cross-linked copolymer obtained from MAA–BA (63 : 37). The following bases have been used: monoethanolamine, diethylamine, and NaOH. From the represented data it is apparent that viscosity of aqueous solutions significantly increases at the neutralization degree of acidic groups equaling 30–40 %, after which it just as significantly decreases. Besides, the position of the viscosity maximum and the intensity of thickening depend on the nature of a neutralizing agent, especially in the range 20–40 % neutralization degree.

On the basis of the obtained data complex the recommended conditions for the synthesis of MAA–BA copolymer thickeners, to be used in aqueous systems, have been chosen: the solvent is cyclohexane, the ratio MAA : BA = 67:33, the initial total concentration of monomers equals 12 % m/m, the initiator concentration (lauroyl peroxide) is 1.0 % mol, the cross-linking agent (DMEG) is present in the amount

0.6 % mol (of $\Sigma[M]_0$). The neutralizing agent and the neutralization degree of acidic units should be chosen individually for each application object.

Other type of polyacryl thickeners, studied in the present paper, has been the lightly cross-linked water-soluble polymers of acrylic acid. In view of the abovementioned literature data, the thickening properties of the polymers on the AA basis were determined in low-freezing aqueous solutions of glycerol and PG, in order to evaluate the possibilities of using such polymers to produce DIF of type IV. The important property of such DIFs is their decreasing viscosity, when an aircraft gathers speed during takeoff, which facilitates the removal of DIF from the hull surface.

That's why the main criteria for comparison of various thickeners are achievement of the optimal level of dynamic viscosity and the degree of its decreasing under mechanical load.

First of all the study has concerned the influence of the type and concentration of the cross-linking agent on the thickening properties of AA homopolymers, obtained by precipitation polymerization in ethyl acetate. As indicated by Table 1, the homopolymer obtained without any cross-linking agent shows a low thickening degree (200 mPa·s) even at its high concentration in the solution, namely, 1.0 % m/m. Low viscosity persists also for the solutions on the basis of the AA homopolymer obtained at insignificant (0.06 % mol of $\Sigma[M]_0$) concentration of the cross-linking agent, which is TGM-3. The observed data point at low molecular masses of the synthesized thickeners. However, with increasing TGM-3 concentration at the synthesis stage up to 0.3 % mol of $\Sigma[M]_0$, the formed polymer has high thickening ability, and the dynamic viscosity of the thickening agent solutions in the media water-glycerol and water-PG equals 7600 and 6700 mPa·s, respectively. Further increase of cross-linking content in the polymer makes it insoluble in the mentioned systems (Table 1, no. 3). As an alternative cross-linking agent, DMEG has been tested, but in this case the obtained polymers have lower thickening ability compared to the samples linked by TGM-3.

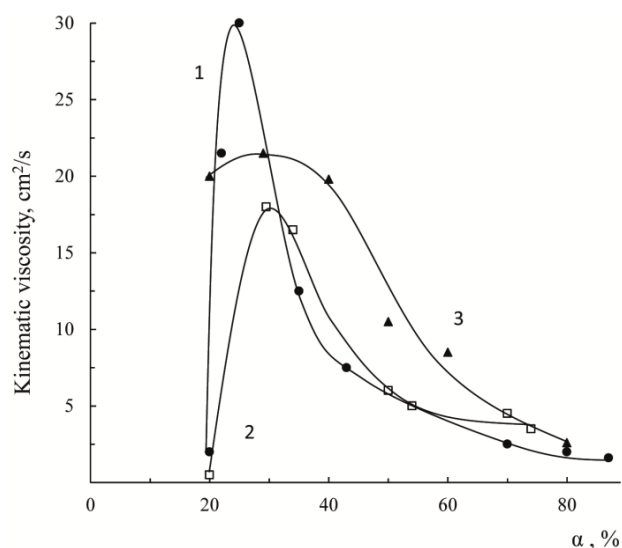


Fig. 4. Kinematic viscosity of the MAA-BA copolymer (63:37) as the function of the neutralization degree of acidic units by monoethanolamine (1), diethylamine (2), and NaOH (3)

Table 1

Synthesis conditions and characteristics of solutions of the polymer thickeners on the basis of acrylic acid

No.	Comonomer (% mol)	Cross-linking agent (% mol of $\Sigma[M]_0$)	Solvent for synthesis	Solvent for testing SPL	C, % m/m	Dynamic viscosity*, mPa·s
1	–	–	Ethyl acetate	Glycerol – water	1.0	200
2	–	TGM-3 (0.30)	Ethyl acetate	Glycerol – water	0.4	7600
				PG – water	0.9	6700
3	–	TGM-3 (0.50)	Ethyl acetate	Glycerol – water	0.4	insoluble
4	–	DMEG (0.30)	Ethyl acetate	Glycerol – water	0.4	7000
				PG – water	0.9	5000
5	AAm (5.0)	TGM-3 (0.30)	Ethyl acetate	Glycerol – water	0.4	900
				PG – water	0.9	200
6	BA (5.0)	TGM-3 (0.30)	Ethyl acetate	Glycerol – water	0.4	6500
				PG – water	0.9	4000
7	LMA (0.5)	TGM-3 (0.20)	Ethyl acetate	Glycerol – water	0.4	5500
				PG – water	0.9	7700

* 0,3 rpm, pH 7.7–8.0.

Organometallic chemistry

The next stage has centered on studying the properties of AA copolymers, linked by TGM-3 and containing additional hydrophobic or hydrophilic fragments. As hydrophobic comonomers at polymerization, butyl acrylate (BA) and lauryl methacrylate (LMA) have been used, while acrylamide (AAm) has been used as the hydrophilic one. The data collected in Table 1, obtained after the testing the abovementioned copolymers in the mixtures water-glycerol and water-PG, show that they are characterized by lower values of dynamic viscosity compared to the linked AA homopolymer. It is particularly remarkable that, as a whole, the obtained laboratory samples thicken the aqueous solutions of glycerol better than the aqueous solutions of PG. This may be explained by better dissolving capacity of the mixture glycerol–water in relation to the obtained polymers, which leads to increasing the size of macromolecular coils in solutions. The given fact points at the preference of using aqueous solutions of glycerol with the thickeners of this type.

Note that for the solutions of almost all obtained polymers (except those with the viscosity value lower than 1000 mPa·s) the pseudo-plastic flow curve under load is typical (Fig. 5).

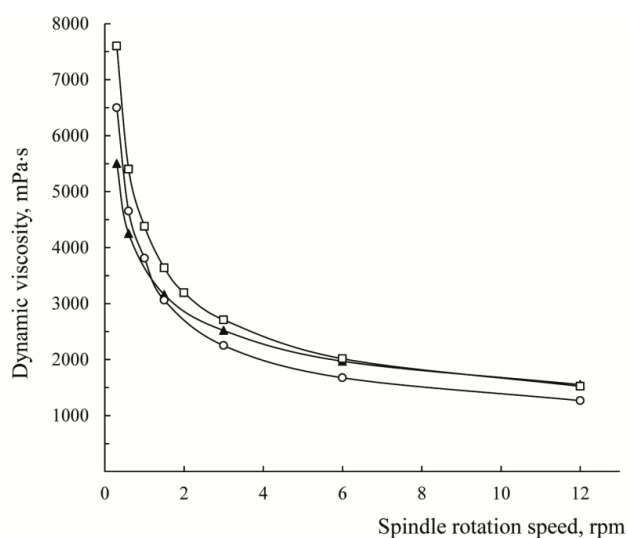


Fig. 5. Dynamic viscosity of water-glycerol solutions of the synthesized thickeners as the function of the spindle rotation speed. Copolymer composition; mass percentage of polymers in the mixture, %; thickener content in the polymer, % mol: (▲) AA:LMA (99.5:0.5), 0.4 %, 0.2 %; (◻) AA, 0.4 %, 0.3 %; (○) AA:BA (95.0:5.0), 0.4 %, 0.3 %

In order to evaluate this effect quantitatively, the degree of pseudo-plasticity has been determined as the ratio of the dynamic viscosity of a solution at the spindle rotation speed 0.3 rpm to the dynamic viscosity of the same solution at the spindle rotation speed 1.5 rpm. Comparative analysis has shown that the pseudo-plasticity effect is the most pronounced for solutions on the basis of the cross-linked AA homopolymer (Table 1, no. 2). The average value of the pseudo-plasticity degree of this polymer, both in the mixture water–glycerol and in the mixture water–PG, equals 2.15; while other thickeners do not reach 2.0 of this value.

Thus, under the chosen experimental conditions the AA homopolymer with the optimal cross-linking degree is found to be the most efficient potential thickener for antifreezing compositions intended for producing DIF of type IV, since its solutions are distinguished by the greatest viscosity and the pseudo-plasticity degree compared to solutions of other investigated thickeners.

Conclusion

Lightly cross-linked polymer thickeners on the basis of acrylic and methacrylic acid have been synthesized with the use of radical precipitation polymerization. For MAA–BA copolymers the influence of cross-linking degree, content of acidic units, the nature of the neutralizing agent, neutralization degree of acidic units upon thickening properties in aqueous solutions has been determined. For cross-linked AA homopolymers fine prospects to be of use as thickeners for DIF of type IV on the basis of water–glycerol solutions have been shown.

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СИНТЕЗ ПОЛИАКРИЛОВЫХ ЗАГУСТИТЕЛЕЙ МЕТОДОМ ОСАДИТЕЛЬНОЙ РАДИКАЛЬНОЙ ПОЛИМЕРИЗАЦИИ

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Методом радикальной осадительной полимеризации синтезированы слабосшитые полимерные загустители на основе акриловой и метакриловой кислот. Определено влияние введения гидрофобных звеньев, степени сшивки, природы нейтрализующего агента, степени нейтрализации кислотных звеньев и других факторов на загущающие свойства полученных полимеров в воде, а также смесях воды с глицерином или пропиленгликолем.

Ключевые слова: акриловая кислота, метакриловая кислота, алкил(мет)акрилаты, радикальная полимеризация, слабосшитые полимеры, загустители, вода, глицерин, гликоли.

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