Synthesis of Methylacrylate and Acrylic Acid Copolymers and Their Application as Materials for Restoration

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Abstract   The radical mechanism was used to synthesize copolymers of methylacrylate and acrylic acid in the bulk and dioxane. By regulating the composition of the copolymer, macromolecules with both hydrophilic and hydrophobic properties were obtained. It was shown that the obtained copolymers satisfy the basic criteria required for the application in the practice of restoration of archaeological objects of different nature.

Keywords   Methylacrylate, Acrylic acid, Radical copolymerization, Copolymer composition solubility, Archeological object, Model

1. Introduction

Copolymers of methylacrylate (MA) and acrylic acid (AA) have been known for a long time [1, 2]. However, there is a little information about the properties of these copolymers and the ways of their practical application. By regulating the synthesis conditions, copolymers can be synthesized in a fairly wide range of compositions. The combination in the macromolecular chain of monomer links containing the group - COOH and - O-CH$_3$ makes it possible to obtain materials in a wide range of hydrophilic-hydrophobic properties. This opens interesting ways of practical application of this copolymer in the practice of restoration and conservation of archaeological objects. It is known, that polybutylmethacrylate, in particular, is widely used for these purposes [3, 4].

Copolymers of acrylic monomers such as butylacrylate and methylacrylate to exhibit adhesive properties to various surfaces (stainless steel, polyethylene, glass and Si-wafer), what makes it possible to use them as pressure sensitive adhesives [5].

Copolymerizations of unsaturated compounds with different ratios of methacrylic monomers (Methylmethacrylate, Butylmethacrylate) exhibit good adhesion, flexibility and waterproofing performance may be used in the paint industry [6].

Different copolymers of hydroxyethyl acrylate and methyl methacrylate were synthesized by solution polymerization using azo-bis-(isobutyronitrile) (AIBN) as initiator and dimethylformamide as a solvent. The copolymers exhibited good thermal stability, flexibility, and adherence [7].

There is also information that the copolymers MA:AK successfully tested in the practice of paper restoration [8, 9].

In this paper has shown the possibility of synthesis of statistical copolymers MA and AA of different compositions and shows the perspectives of their practical application for archaeological objects restoration.

2. Experimental

During of investigations used industrial monomer MA produced "NAVOIYAZOT" JSC (Uzbekistan) and ice AA produced HIMEDIA Laboratories (India). The monomers were rectified by vacuum distillation.

The distilled monomers had the following characteristics:

Monomer	Boiling point, T$_B$, °C	Density, D$_4^{20}$, g/cm^3	Refractive index, n$_d^{20}$
MA	80,3	0,956	1,404
AA	141,6	1,051	1,422

Copolymers were synthesized in a flask placed in a water bath in a nitrogen atmosphere, in the presence of azobis (isobutyronitrile) (AIBN) as initiator at 60°C. Reprecipitation of the polymers was performed with hexane.

The composition of the copolymer was determined by elemental analysis by titration of carboxylic groups.

IR spectra have been recorded using Specord 75 IR spectrometer. The samples were in the form of films or tablets with KBr.

Intrinsic viscosities of polymer solution were measured by using Ubbelohde viscosimeter [10].

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3. Results and Discussion

3.1. Synthesis of Copolymers

Both AA and MA relates to the active monomers, because they have in their composition a carbonyl group directly associated with a double bond. In the structure of monomers, π–π conjugation is realized, which increases the reactivity of the double bond. Both monomers have a positive polarity factor **e**, which indicates a positive charge on the β-carbon double bond atom.
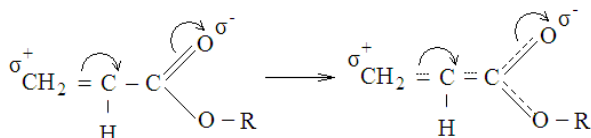
were R: – H or CH$_3$

Synthesis of the copolymers of MA and AA in the solution of dioxane and in the bulk was carried out.

Figure 1 shows the dependence of the copolymer composition on the molar ratio of the monomers in the initial reaction mixture.
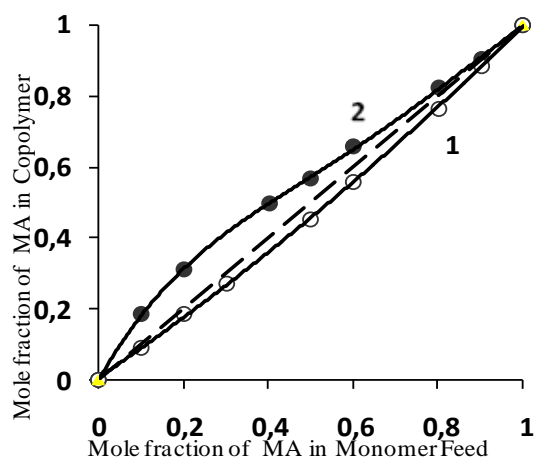

Figure 1. Schematic Representation of the Copolymers composition vs. Monomer Feed in dioxane (1) in bulk (2). [AIBN]= $6.8*10^{-3}$, T= 60℃. Yield< 10%

Copolymerization constants were calculated from the obtained data:

Reaction medium	MA	AA
dioxane	$r_1 = 0,95$	$r_2 = 0,40$
bulk	$r_1 = 0,85$	$r_2 = 1,12$

The difference in the copolymerization constants of AA in the bulk and in dioxane could be explained as follows. It is known that AA in the bulk there is a dimer of the following structure [2]:
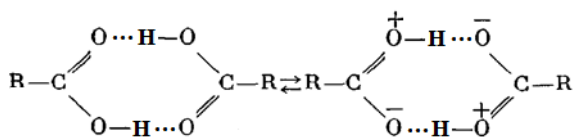
According literature it is known that π - electrons of the carbonyl group closing the conjugation system can participate in the hydrogen bond, and π - electron cloud can be transferred through the hydrogen bond. In dimeric ring formed is common to both molecules of conjugation circuit. Therefore, in the dimers of AA, a double bond in a greater degree associated with π - electronic system of the substituent and an unpaired electron in the corresponding radical is largely delocalized than in the "isolated" AA molecules. This is confirmed by the fact, that the Q-factor (resonance stabilization factor) characterizing the degree of conjugation of the double bond with the substituent in AA dimers is greater than in the complexes of the same acid with the solvent. Indeed, according to [2], the value of resonance stabilization factor for AA in bulk $Q_{AA}=0.7$, in the solution $Q_{AA} =0.15$. These data indicate that during polymerization in the solvent, the AA dimer is destroyed, which leads to decrease of the resonance stabilization factor and, accordingly, to decrease of the AA copolymerization constant. In the copolymerization in dioxane $r_1< 1$ and $r_2< 1$, so the dependence (Fig. 1) crosses the azeotrope line at the molar ratio MA:AA ~ 95:5. From the dependencies shown in Fig. 1 it follows an important conclusion. For almost any composition of the monomer mixture, can be chosen a solvent concentration at which the composition of the copolymer will coincide with the composition of the monomer mixture. In this case, the composition of the monomer mixture don't change with increasing conversion, which contributes to the production of copolymers with high homogeneity in composition, since the conversion component of the composite heterogeneity is excluded.

The synthesized copolymers were also characterized by IR spectroscopy (Figure 2).
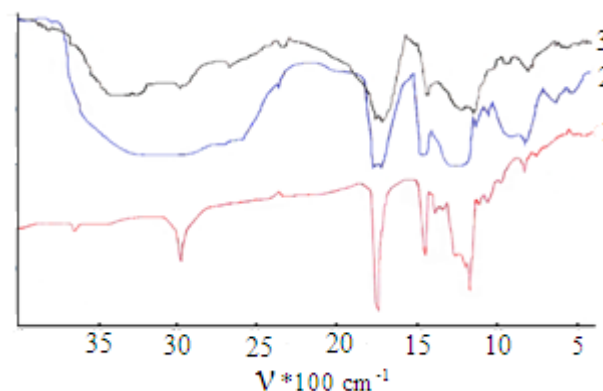
Figure 2. IR - spectra of poly-MA(1), poly-AA (2), MA:AA copolymer (3)

In the IR- spectrum of Poly MA, an absorption band at 1120 cm^{-1} is observed, characterizing the presence of C-O-C bonds in the ester group. At 1420 cm^{-1}, the absorption band of the methyl group associated with the oxygen atom is observed. The presence of a carbonyl group of a ester bond is revealed in the form of an absorption band at 1710 cm^{-1}.

In the IR- spectrum of Poly AA there is a wide absorption band in the region of 3300-2500 cm^{-1} characterizing the

valence oscillations of hydroxyl groups involved in intermolecular and intramolecular hydrogen bonds, respectively. At 1680-1620 cm^{-1} there are absorption bands C=O groups. Deformation vibrations of CH_2 adjacent to C=O groups occurred at 1420, 1310 cm^{-1}. At 980 cm^{-1}, pendulum oscillations of CH_2 groups were observed.

IR spectra of copolymers MA:AA has shown that in all samples the main absorption bands of acrylic acid and methylacrylate are persisted, since the main absorption bands remain unchanged at 1740-1680 cm^{-1} C=O. IR spectra of copolymers largely correspond to the additive superposition of the spectra of the homopolymers [11, 12].

3.2. Copolymers Solubility

MA: AA copolymers have different solubility depending on their composition. Samples containing more than 50% AA at room temperature do not dissolve in DMFA, but are well soluble in water, ethanol and dioxane. Samples which contain in their composition 50% or less of AA, easily soluble in dioxane and DMFA. Thus, copolymers, depending on their composition, have different affinity to solvents. We also investigated the influence of the composition of the copolymer in their intrinsic viscosity ([η]) in a mixture of solvents acetone : water (Table 1).

Table 1. Intrinsic viscosity of copolymers synthesized at different ratios of MA:AA monomers in different solvents. [I]= 6.8*10^{-3}mol / l; T= 25℃

№	Ratio of monomers, mol. %		Intrinsic viscosity of copolymers in a mixture of solvents acetone: water, [η], dl/g		
	MA	AA	80:20	50:50	20:80
1	20	80	2,52	2,36	2,17
2	50	50	1,82	1,26	insoluble
3	80	20	1,30	insoluble	insoluble

As can be seen from the results, the intrinsic viscosity of the copolymers depends on the composition of the solvent. Increasing of the water content in the solvent leads to change in the conformation of macromolecules, consisting in decreasing of the size of the tangle. The same phenomenon leads to increase in the proportion of MA in the copolymer. Moreover, the composition of the copolymer also has a significant impact on the nature of the change in the size of the tangle. For a copolymer with high AA content, when the solvent composition changes, the intrinsic viscosity does not change as significantly as for a copolymer with an equimolar composition. A copolymer with high content of MA is not soluble in equimolar solution of acetone-water.

The influence of the copolymer composition on the intrinsic viscosity in dioxane at 30℃. In this solvent soluble copolymers of different composition of MA:AA (Table 2).

The intrinsic viscosity of copolymers synthesized at the ratio of monomers MA: AA = 1: 4 is slightly lower than that of other samples. However, in general, there is no distinct dependence [η] on the composition of the copolymer. This result is quite expected, based on the close values of the

copolymerization constants r$_1$< 1 and r$_2$< 1.

Table 2. Compositions and intrinsic viscosity ([η]) of MA:AA copolymers synthesized at different ratios of monomers

№	Concentration of monomers, Mol/l		Copolymer composition, mol. %		[η], dl/g
	[MA]	[AK]	MA	AK	
1	0,5	4,5	18,60	81,40	0.48
2	1,0	4,0	31,30	68,70	0.36
3	2,0	3,0	49,65	50,35	0.54
4	2,5	2,5	56,7	43,3	0.43
5	3,0	2,0	65,65	34,35	0.42
6	4,0	1,0	82,3	17,7	0.50
7	4,5	0,5	90,2	9,8	0.47

Thus, by regulate the synthesis conditions, copolymers can be synthesized in a fairly wide range of compositions. The presence of such different monomers in the chain leads to the fact that copolymers with different compositions will behave differently in solvents of different nature. In our opinion, the fact that by varying the composition of the copolymer it is possible to obtain materials in a wide range of hydrophilic-hydrophobic properties opens interesting ways of practical application of this copolymer in the practice of restoration and conservation of archaeological objects.

3.3. Experiments on Models of Archaeological Objects

Polymer materials used for the restoration of archaeological objects should satisfy a number of criteria. First of all, it should provide an increase in the strength of objects. Also, it should not change the appearance of the object. The surface after treatment should not look like lacquered. It is also important that the polymer retains its linear structure for a long time so that it can be removed from the object by dissolving.

Table 3. Mechanical strength of models impregnated with solutions of copolymers MA: AK of different composition. The mechanical strength of the not impregnated models σ$_0$ = 4,4 MPa

№	Ratio of monomers, mol. %		The average mass fraction of polymer in the models, %	Mechanical strength, σ, MPa
	[MA]	[AA]		
1	100	-	0,313	5,62± 0,45
2	40	60	0,313	7,73 ± 0,37
3	50	50	0,33	8,70 ± 0,59
4	60	40	0,30	9,71± 0,02
5	80	20	0,335	7,50± 0,21
6	90	10	0,323	7,95±1,58

The obtained MA:AA copolymers were tested on models of archaeological objects. The models are samples in the form of cubes made of a mixture of sand and clay in the ratio sand:clay = 3:7 by pressing and then drying at room temperature to a constant mass. Copolymers were dissolved in acetone. Concentration of solutions up to 5%. The copolymer solutions were then applied with a brush to the

models, dried to a constant mass, and then tested for mechanical strength. The experiments were carried out on the ZWICK testing machine, adapted to the press.

Table 3 shows the dependence of the mechanical strength of models (σ) on the composition of the copolymer by which they were impregnated. The average polymer mass applied to the model was 0.090 ±0.011 g.

Figure 3 shows the effect of the amount of impregnated copolymer on the mechanical strength of models of archaeological objects. For comparison, a similar dependence for polybutylmethacrylate, which is used for the restoration and conservation of archaeological objects has shown.
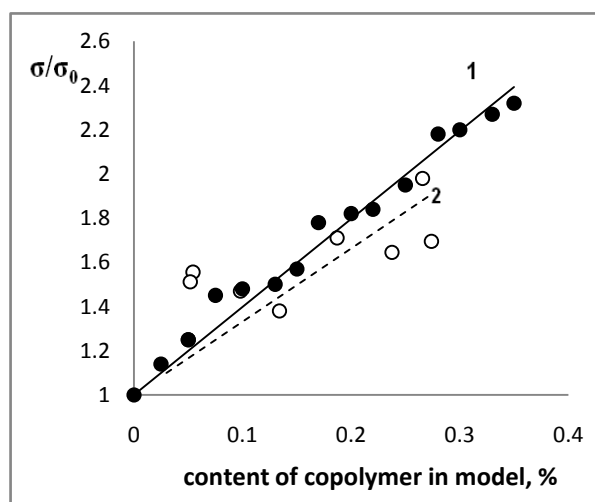
Figure 3. Dependence of mechanical compressive strength of models on the content of copolymer MA: AK (1) and polybutylmethacrylate (2). The results for polybutylmethacrylate are taken from [4]. Table 4 shows a comparison of the properties of poly-BMA and MA:AA copolymer

Table 4. Compares the properties of polymers for their application as materials for restoration

properties	Poly-BMA	MA:AA copolymer
Structure	$-[-CH_2 - C-]_n-$ with CH_3, $C=O$, O, C_4H_9	$-[CH_2-CH-]_n-[CH_2-CH-]_m-$ with $C=O$, O, CH_3 and $C=O$, O, H
Increasing of mechanical strength	1.8-2.0 times	2.0-2.2 times
water resistance	waterproof	The property can be regulated by changing the composition of the copolymer
possibility of removed	removed by dissolving	removed by dissolving
Surface character	lack of gloss	lack of gloss

As can be seen from the figure 3, the mechanical strength of models impregnated with solutions of copolymers MA:AA increases with growing their mass fraction.

Moreover, this effect for copolymers of MA:AA is expressed even stronger than for polybutylmethacrylate. Copolymer, penetrating into the pores of the object, glues the material particles and thus increases their mechanical strength.

Was also evaluated the possibility of deleting the copolymers from the objects. For this, models, impregnated with a solution of a copolymer over a month ago, were purified with acetone. Next, the acetone solution was precipitated in hexane. In this case, precipitation of the copolymer was observed. This indicates that copolymers retain a linear structure and can be removed from objects by solvent.

4. Conclusions

Thus, in the conditions of radical initiation the copolymers MA and AA of different composition were synthesized. It is established that the copolymer MA: AA has all the basic criteria necessary for its application in the practice of restoration of archaeological objects. Impregnation of models with copolymer solutions leads to an increase in their mechanical strength. In this case, the copolymer retains the linear structure and can be removed from the object if necessary.

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