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## MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

# Thermomechanical Properties and Heat Resistance of Copolymers of Methyl Methacrylate with Acrylic Acid

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**Abstract**—Copolymers with a mole fraction of acrylate units of 0.20 to 0.69 were prepared by radical copolymerization of methyl methacrylate with acrylic acid. The heat resistance and thermomechanical properties of copolymer films formed from dimethylformamide solution were evaluated, and the possibilities of improving these characteristics were demonstrated.

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Thanks to high light transmittance, polymeric compounds based on poly(methyl methacrylate) (PMMA) are widely used in optical systems for information recording, but their applicability is restricted by the relatively low glass transition and flow points of methyl methacrylate (MMA) polymers and the insufficient adhesion of the material to silicate glasses. In this context, an urgent problem is modification of PMMA properties with the aim to improve its thermomechanical properties and enhance the heat resistance and adhesion, with preservation of the optical transparency. It has been found previously [1, 2] that materials with the required characteristics can be obtained by radical copolymerization of MMA with acrylic acid (AA). However, the dependence of the properties of the copolymers (CPs) on their composition has not been studied.

In this study we examined how the composition of MMA–AA copolymers affects their thermal properties.

## EXPERIMENTAL

Radical copolymerization in the bulk was performed in a nitrogen flow at 60°C for 4 h in a glass test tube equipped with a reflux condenser [3]. The AA : MMA molar ratio was varied from 1 : 4 to 4 : 1. As initiator we used 2,2'-azobis(isobutyronitrile). After the synthesis completion, the polymer sample was ground and washed at room temperature with water and ethanol to remove the unchanged monomers and a part of AA homopolymer. Then the sample was dried and dissolved in dimethylformamide (DMF). The solution was passed through a glass frit, after which the copolymerization product was precipitated from the solution into water. A small amount of PMMA, which is insoluble in DMF, remained on the filter. The AA homopolymer remained in the CP precipitant. The CP composition was determined by acid–base titration of carboxy groups in organic solvents.

Poly(methyl methacrylate) and polyacrylic acid (PAA) were prepared under the same conditions as the MMA–AA copolymer. The molecular weights (MW) of PMMA and PAA were determined viscometrically in trichloromethane at 25°C ($K = 0.48 \times 10^{-4}$, $a = 0.80$; MW = $3.85 \times 10^5$) and in water at 30°C ($K = 7.6 \times 10^{-4}$, $a = 0.5$; MW = $1.62 \times 10^6$), respectively. To estimate the lengths of molecular chains in CPs of various compositions at 25°C, we measured the specific viscosities of their 0.5% solutions in a common solvent, acetic acid.

The thermal properties of the CPs were studied using film samples prepared from DMF solutions. Because of the high adhesion to glass, the films could not be detached from glass supports. Therefore, when preparing film samples for studying the thermal properties of the CPs, we used as supports polypropylene plates. After solvent evaporation, transparent polymer films were obtained. They could be readily separated from the surface of the polypropylene plates. To remove residual DMF, the films were repeatedly washed with distilled water.

The thermal properties of MMA–AA were studied by the methods of combined thermal and thermomechanical analysis. A combined thermal analysis was performed on an OD-103 derivatograph (MOM, Hungary). The TG, DTG, and DTA curves were recorded in air at a heating rate of 5 deg min$^{-1}$. The sample weight was 100 mg. From the TG curves, we determined the temperatures $T_5$ and $T_{10}$ corresponding to 5 and 10% weight loss, respectively. From the position of the minimum in the DTG curves, we determined the temperature of the maximal degradation rate, $T_m$.

The thermomechanical analysis was performed with a UIP-70 device (Central Design Office with Pilot Plant, USSR Academy of Sciences) in air at the same heating rate. A pressure of 0.59 MPa was applied to the sample. The film thickness was 50–90 μm. The thermomechanical properties were evaluated from the curves of the relative punching strain ε (%) vs. temperature $T$ (°C).

Analysis of the chemical composition of the CPs (Table 1) showed that it coincided with the composition of the monomer mixture up to AA mole fraction in the mixture equal to 0.2. With a further increase in the AA content of the monomer mixture, the CP became depleted of AA units.

Solubility tests of the CPs in various organic solvents (acetone, ethanol, 1,4-dioxane, aromatic and chlorinated hydrocarbons, acetic acid, DMF) showed that the CPs dissolve to give concentrated solutions only in DMF and glacial acetic acid. Poly(methyl methacrylate) forms in these solvents only dilute solutions.

**Table 1.** Resistance of MMA–AA copolymers to thermal oxidative degradation

| Mole fraction | | $T_5$ | $T_{10}$ | $T_m$ |
|---|---|---|---|---|
| AA in monomer mixture | AA units in CP | °C | | |
| 0 | 0 | 161 | 182 | 283 |
| 0.2 | 0.20 | 239 | 267 | 390 |
| 0.3 | 0.24 | 240 | 272 | 380 |
| 0.4 | 0.28 | 259 | 280 | 387 |
| 0.5 | 0.34 | 240 | 270 | 380 |
| 0.6 | 0.40 | 233 | 261 | 375 |
| 0.7 | 0.60 | 161 | 185 | 380 |
| 0.8 | 0.69 | 135 | 168 | 380 |
| 1.0 | 1.0 | 131 | 159 | 255 |

Figure 1 shows that, as the mole fraction of AA units in the CP is raised to approximately 0.3 (monomer molar ratio AA : MMA = 1 : 1.5), the specific viscosity of the CP increases relative to PMMA. As the mole fraction of AA units is raised further, the viscosity decreases, and, at the mole fraction of AA units equal to 0.69, becomes equal to the specific viscosity of PAA. Apparently, variation of the monomer ratio in the course of the CP synthesis was accompanied by variation of not only the chemical composition but also the polymer chain length, with the maximal chain length attained at approximately equimolar ratio of the monomers.

The thermogravimetric curves of MMA and AA homopolymers and of MMA–AA copolymers of various compositions (Fig. 2) show that the weight

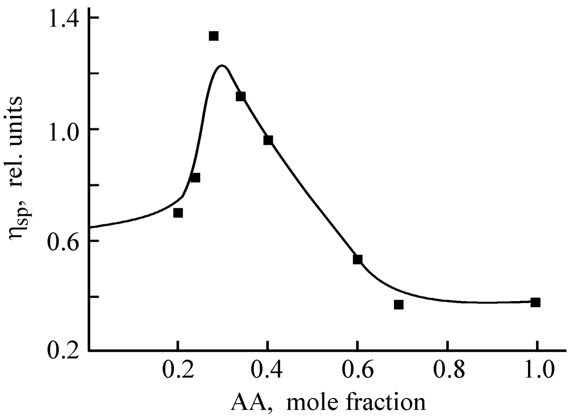

**Fig. 1.** Specific viscosity $\eta_{sp}$ of 0.5% solutions of homo- and copolymers of MMA and AA in acetic acid vs. the mole fraction of AA units in CP.

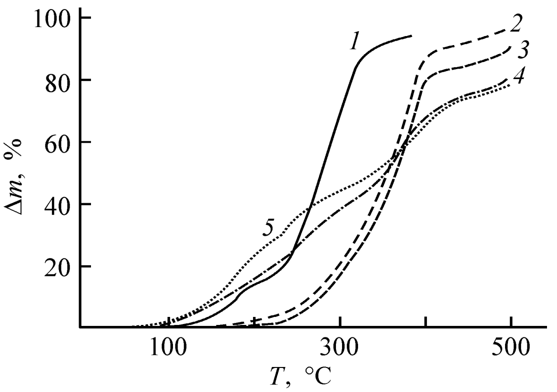

**Fig. 2.** Weight loss $\Delta m$ vs. temperature $T$ in thermal gravimetric analysis of (*1*) PMMA, (*2–4*) MMA–AA copolymers, and (*5*) PAA. Mole fraction of AA units in CP: (*2*) 0.20, (*3*) 0.28, and (*4*) 0.69.

**Table 2.** Glass transition and flow points of MMA–AA copolymers

| Mole fraction of AA units in CP | $T_g$ | $T_f$ |
|---|---|---|
| | °C | |
| 0 | 76 | 168 |
| 0.28 | 72 | 212 |
| 0.34 | 93 | 230 |
| 0.40 | 64 | 130 |
| 1.0 | 85 | 160 |

loss by the CPs may be either smaller or larger than the weight loss by the homopolymers, depending on the composition and temperature. For example, the weight loss by the CPs with the mole fraction of AA units equal to 0.20 and 0.28 (curves *2* and *3*, respectively) in the range from room temperature to 365–370°C is lower than the weight loss by PMMA (curve *1*) and PAA (curve *5*), and only at temperatures exceeding 370°C, the weight loss by the CPs becomes larger, compared to PAA, but remains smaller, compared to PMMA. At the mole fraction of AA units in the CP equal to 0.69, the weight loss in the range from 100 to 240–250°C (curve *4*) is smaller, compared to PAA (curve *5*), but larger, compared to PMMA (curve *1*). In the temperature range 250–500°C, the weight loss by the CP with a high content of AA units is smaller than that by PMMA and similar to that by PAA.

Thus, the CP with a relatively low content of AA units is the most resistant to thermal oxidative degradation. The observed effect is apparently associated with the decreased efficiency of cleavage of chemical bonds in the CP backbone, due to changes in the chemical nature of pendant functional groups in going from the homopolymers to CP. The low resistance to thermal oxidative degradation of the CP with a high content of AA units, compared to PMMA, in the range of up to 250°C is apparently caused by the possible decarboxylation of relatively long blocks of AA units. At temperatures exceeding 250–260°C, when the decarboxylation is complete and the observed weight loss is caused by the cleavage of chemical bonds in the CP backbone, the enhanced resistance of the copolymers to thermal oxidative degradation, compared to PMMA, is clearly manifested.

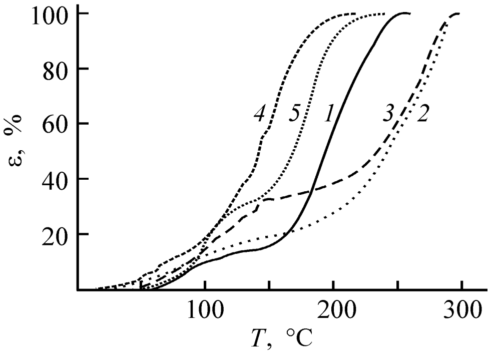

**Fig. 3.** Thermomechanical curves of (*1*) PMMA, (*2–4*) MAA–AA copolymers, and (*5*) PAA. (ε) Strain and (*T*) temperature. Mole fraction of AA units in CP: (*2*) 0.28, (*3*) 0.34, and (*4*) 0.40.

Data on the resistance of MMA–AA copolymers to thermal oxidative degradation ($T_5$, $T_{10}$, $T_m$) in relation to their composition are listed in Table 1. It can be seen that MMA and AA homopolymers show similar resistances to thermal oxidative degradation: For PMMA, $T_5$, $T_{10}$, and $T_m$ are 161, 182, and 283°C, and for PAA, 131, 159, and 255°C, respectively. The MMA–AA copolymers with the mole fraction of AA units of 0.20 to 0.40 are more resistant to thermal oxidative degradation than PMMA and PAA. The largest values of $T_5$ and $T_{10}$, exceeding those of PMMA and PAA by almost 100°C, are attained at the mole fraction of AA units in the CP equal to 0.28, i.e., at the same copolymer composition at which the specific viscosity of 0.5% solutions of the CP in acetic acid becomes maximal. With a further increase in the mole fraction of AA units in CP to 0.60 and 0.69, $T_5$ and $T_{10}$ dramatically decrease, approaching the values characteristic of PAA. It is important that the specific viscosity of 0.5% solutions of such CPs in acetic acid also becomes lower than that of the 0.5% PMMA solution. Therefore, apparently, the lower resistance to thermal oxidative degradation of the CP with a high content of AA units, observed in the initial steps of weight loss, may be due not only to possible decarboxylation of long blocks of AA units, but also to increased tendency of shorter CP chains to degrade. A certain contribution to the weight loss may also be made by removal of sorbed moisture whose amount increases with the content of AA units in the CP.

At high temperatures corresponding to active cleavage of chemical bonds in the backbone, the resistance of the CPs to thermal oxidative degradation is virtually independent of their composition. The temperature of the maximal degradation rate, $T_m$, of CPs fluctuates in the range 375–390°C as the mole fraction of AA units in the CP is varied from 0.20 to 0.69, whereas for PMMA, $T_m$ is 283, and for PAA, 255°C.

The thermomechanical curves of PMMA, PAA, and MMA–AA copolymers are shown in Fig. 3, and the temperatures of transitions from one relaxation state to another are listed in Table 2. As can be seen from

Fig. 3, the thermomechanical curve of PMMA is typical of amorphous polymers. The temperature ranges corresponding to glassy, hyperelastic, and viscous-flow states can be distinguished. The temperatures of transitions from glassy to hyperelastic (glass transition point, $T_g$) and from hyperelastic to viscous-flow states (flow point, $T_f$) for PMMA are 76 and 168°C, respectively (Table 2). The thermomechanical curve of PAA is also typical of an amorphous polymer and is characterized by the temperatures $T_g$ and $T_f$ close to those of PMMA: 85 and 160°C, respectively.

The thermomechanical curves of MMA–AA copolymers do not differ essentially from those of PMMA and PAA. However, their position on the temperature scale relative to the curves of the homopolymers depends on the CP composition. The thermomechanical curves of CP samples with a AA mole fraction equal to 0.28 and 0.34 are shifted toward higher temperatures relative to the homopolymers. The glass transition points $T_g$ of the CPs of these compositions are close to those of MMA and AA, whereas the flow points $T_f$ exceed those of the homopolymers by more than 40°C. At the same time, the thermomechanical curve of the CP sample with a AA mole fraction equal to 0.40 is shifted toward lower temperatures, and $T_g$ and $T_f$ become lower than those of the homopolymers. Apparently, the sharp decrease in the flow point of the CP with a AA mole fraction equal to 0.40 is due to the short chain length (Fig. 1).

## CONCLUSIONS

(1) Resistance to thermal oxidative degradation of methyl methacrylate–acrylic acid copolymers with the mole fraction of acrylic acid units of 0.20 to 0.40 exceeds that of the corresponding homopolymers. The heat resistance enhancement takes place for the step of cleavage of chemical bonds in the macromolecular backbone.

(2) The dependences of the glass transition and flow points of the methyl methacrylate–acrylic acid copolymers on the copolymer composition pass through a maximum at the mole fraction of acrylic acid units equal to 0.34.

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