

Poly(Methyl Methacrylate)–Cellulose Nitrate Copolymers. I. Preparation

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Synopsis

Poly(methyl methacrylate)–cellulose nitrate copolymers were prepared in the form of rods and sheets by bulk polymerization using benzoyl peroxide as initiator. Suspension polymerization did not succeed in preparing poly(methyl methacrylate)–cellulose nitrate copolymers, especially when cellulose nitrate of 11.4% nitrogen content was used. The parameters such as cellulose nitrate concentration, nitrogen content of cellulose nitrate, the amount of initiator and the reaction time, and the temperature are discussed. The prepared copolymers were irradiated for specified periods of up to 11.83 Mrad. It was found that poly(methyl methacrylate)–cellulose nitrate copolymers did not dissolve in any conventional solvent, but they swelled. Swelling decreases with increasing cellulose nitrate concentrations, nitrogen content of cellulose nitrate, and irradiation dose, indicating the crosslinked structure of the prepared copolymers.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has received much attention nowadays for its wide uses in many industrial applications. Among these uses are the preparation of graft copolymers with methyl cellulose,^{1,2} natural and modified wool,³ polyester fibers,⁴ etc. to improve their physical, mechanical, and chemical properties. Also, graft copolymers from acrylic monomers (like acrylic acid, methyl methacrylate, ethyl acrylate, and methyl acrylate) and cellulose acetate^{5,6} were prepared for water desalination by reverse osmosis technique. No effort has been made so far to modify cellulose nitrate despite its versatile applications in surface coatings, leathers, and plastics. More recently, cellulose nitrate was grafted by methyl methacrylate monomer in solution using benzoyl peroxide as initiator⁷ to produce cellulose nitrate lacquers and lacquer emulsions which would yield a flexible film of high mechanical properties, high elasticity, good gloss, and high water repellency. Also, cellulose nitrate was grafted by methyl methacrylate and methyl acrylate monomers using ceric ammonium nitrate⁸ as a catalyst to produce lacquers and lacquer emulsions.

The aim of the present work is to prepare different types of poly(methyl methacrylate)–cellulose nitrate (PMMA–CN) copolymers by suspension or bulk polymerization useful in the field of plastics.

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EXPERIMENTAL

Materials

(1) Pure methyl methacrylate (MMA) monomer was freed from inhibitor by washing with aqueous sodium hydroxide solutions (10%) until color-free and with distilled water until alkali-free, dried over anhydrous calcium chloride, and distilled under reduced pressure.

(2) Cellulose nitrate (CN) of 11.4, 12.2, and 13.1% nitrogen content (supplied by Abu-Zaabal Company for Speciality Chemicals, Egypt) was purified by washing with water and dried to constant weight.

(3) BDH benzoyl peroxide was used.

(4) Pure monohydrogen disodium phosphate, dihydrogen monosodium phosphate, and pure soluble starch were used.

(5) *Solvents and chemicals:* All other solvents and chemicals reagents used in this work were at least of chemically pure grade and were further purified and dried as needed by the usual techniques.

Techniques

Preparation of MMA-CN Mixtures

The required amount of dry cellulose nitrate was impregnated in inhibitor-free MMA monomer for 24 hr at room temperature with continuous shaking. The mixture was stored in the dark until air-bubble-free.

Viscosity

The viscosity of the mixtures was measured by Brookfield Synchro-Lectric viscometer. It measures the torque required (in poise) to rotate a cylinder or spindle in the fluid at constant speed.

Preparation of PMMA and PMMA-CN Copolymers

Suspension Polymerization. A solution of soluble starch in distilled water was placed in a three-neck flask. A buffer solution prepared by dissolving disodium monohydrogen phosphate and monosodium dihydrogen phosphate in water was added. Benzoyl peroxide was dissolved in MMA monomer (or MMA-CN mixture) and then added to the contents of the flask. The stirrer was operated at a certain speed that was determined by a speedometer. The flask was heated in a thermostat to complete the polymerization. The polymer was separated by suction filtration. The polymer was then washed several times with warm water and finally dried under reduced pressure at 45°C.

Bulk Polymerization. The bulk polymerization of MMA monomer and MMA-CN mixtures was carried out in sealed ampoules and a cell composed of two glass plates 250 × 250 × 4 mm, separated by PVC tapes 6 mm wide at three sides.

Benzoyl peroxide was dissolved in MMA monomer or MMA-CN mixture in a conical flask. The solution was heated at 90°C for 8 min, then cooled to room temperature. The partially polymerized MMA or MMA-CN mixture was then

poured into the ampoule or the cell in which bulk polymerization was carried out, and allowed to stand until free of air bubbles. Then the ampoule was sealed by fire or the fourth side of the cell was sealed by a PVC tape. The ampoule or the cell was kept in an oven for about 48 hr at a temperature of 36°C, then the temperature was raised to 90°C for a further hour to complete the polymerization. After steady cooling, a rod or sheet of PMMA or PMMA-CN copolymer free of air bubbles was obtained.

Irradiation

Irradiation of the prepared PMMA and PMMA-CN copolymers was carried out in air. The samples were irradiated at 25°C for specific periods at a dose rate of 73 rad/sec by using a ^{60}Co source located at the Regional Centre for Radioactive Isotopes, Cairo.

Swelling Measurements (ref. 9)

The extent of swelling of the prepared copolymers was determined by equilibrating a known weight sample with benzene solvent. Thus, about 0.2 g of each specimen was weighed (W_0) accurately in a weighing bottle, covered with benzene, and left for 24 hr at room temperature. The specimen was removed, blotted quickly with absorbent paper to remove the surface liquid, and then weighed (W_1):

$$\text{Swelling (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

Percent Homopolymer

About 1 g of each sample was accurately weighed (W_0), then extracted in a Soxhlet apparatus using a mixture of benzene and chloroform (1:1 by volume) as solvent, for 72 hr. After extraction, the samples were dried in a vacuum oven at 50°C to constant weight (W_1):

$$\% \text{ homopolymer} = \frac{W_0 - W_1}{W_0} \times 100$$

RESULTS AND DISCUSSION

Different concentrations of dry CN of 11.4, 12.2, and 13.1% nitrogen content were impregnated in MMA monomer for 24 hr at room temperature with continuous shaking. The maximum solubility of cellulose nitrates was found to be 6, 4, and 1%, respectively.

Viscosity of MMA-CN Mixtures

The viscosity of MMA-CN mixtures (assumed as Newtonian fluids) was measured at 25°C before the addition of the initiator. Figure 1 shows the effect of cellulose nitrates concentrations on the viscosity of their mixtures with MMA monomers.

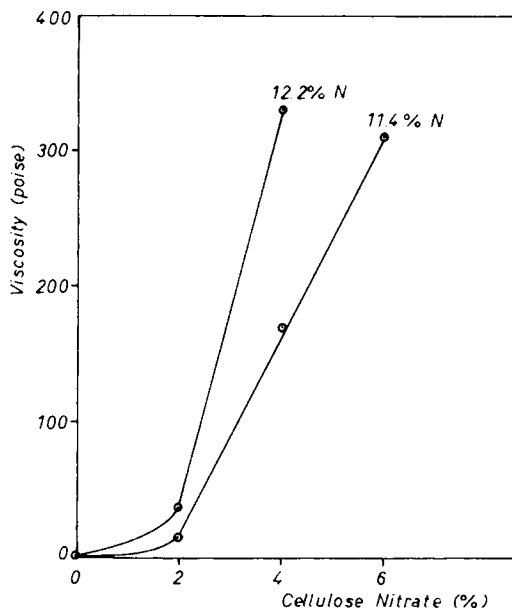


Fig. 1. Viscosity of MMA-CN blends.

It can be shown from Figure 1 that the viscosity of the mixtures increases sharply with the increase of CN concentration in the mixture. Moreover, the viscosity increases in higher rates with nitrogen content.

Preparation of PMMA and PMMA-CN Copolymers

SUSPENSION POLYMERS

PMMA granules were previously prepared by suspension polymerization with sufficiently narrow molecular weight distribution and good enough flow properties for injection molding. It is interesting to prepare PMMA-CN copolymers in the same way. In order to obtain preliminary data regarding suspension polymerization of MMA-CN mixtures, the following runs were carried out.

PMMA

MMA monomer, 50 g containing 0.5 g benzoyl peroxide were added to 150 ml of 1% soluble starch solution and a buffer solution (0.85 g Na_2HPO_4 and 0.05 g NaH_2PO_4 dissolved in 5 ml of distilled water). The stirrer was operated at a speed of 1500 rpm. The flask was heated to 80–85°C for 2.5 hr. The PMMA was obtained as fine beads, washed with water, and dried under reduced pressure. The average conversion was 89.85%.

PMMA-CN (11.4% N) Copolymers

In order to obtain preliminary data regarding suspension polymerization of MMA-CN mixtures, the following runs were performed in the same manner as in PMMA.

PMMA-CN Copolymer of 2% CN:

(1) MMA-CN mixture containing 1% benzoyl peroxide was added to soluble starch and buffer solution. The reaction conditions were time, 2.5 hr; temperature, 80–85°C; and speed of stirring, 1500 rpm. The obtained copolymer was coagulated around the stirrers shaft.

(2) Another experiment was made under the same experimental conditions mentioned before, but the temperature was maintained at 75–80°C. The obtained products were coarse, white, hard beads and flakes.

(3) In the third experiment, the reaction time was reduced to 2 hr, whereby copolymer beads and flakes of indefinite shapes and sizes were obtained.

(4) Two other experiments were performed to find out the effect of stirring speed on the shape of the beads. The reaction conditions were time, 2 hr; temperature, 75–80°C.

The product was more or less regular flakes at 1750 rpm and spherical granules of different sizes at 2000 rpm.

PMMA-CN Copolymer of 4% CN:

Two experiments were chosen from this series of experiments. In the first, the reaction conditions were time, 2 hr; temperature, 75–80°C; and speed of stirring, 2000 rpm. But in the second experiment the temperature was reduced to 70–75°C.

The products of both experiments were flakes and beads of irregular shapes.

PMMA-CN Copolymer of 6% CN:

A series of experiments was made. The reaction conditions (reaction time, temperature, the amount of catalyst, and speed of stirring) were studied in detail. In all runs, beads and flakes of PMMA-CN copolymers of indefinite shapes were obtained.

PMMA-CN (12.2% N) Copolymers

Suspension polymerization succeeded in preparing fine beads of definite shape of PMMA-CN (12.2% N) copolymers for both 2 and 4% CN concentrations. The reaction conditions were time, 2 hr; temperature, 75–80°C; amount of initiator, 1% on the weight of MMA-CN mixture; and speed of stirring, 2000 rpm.

The average conversion was 89.87% when the mixture containing 2% CN, while it was 90.08% for that containing 4% CN.

*BULK POLYMERIZATION OF MMA-CN MIXTURES**PMMA*

MMA monomer containing 1% initiator was polymerized by bulk polymerization. At first, the reaction was carried out in sealed ampoules under refined CO₂ by heating at 90°C for 8 min and then rapidly cooling to room temperature in a water bath. After cooling, the ampoules was heated to 40°C for 48 hr. To ensure complete polymerization, the temperature was raised to 90°C and the heating was continued for an additional hour.

In a second step, water white sheets of PMMA, free of air bubbles, 250 × 250 mm were prepared under the same conditions mentioned before.

PMMA-CN Copolymers

PMMA-CN (11.4%) Copolymers:

The conditions used in preparing PMMA failed in this case, but transparent rods and sheets, free of air bubbles, were obtained when the reaction temperature was reduced to 37°C for the three CN concentrations (2, 4, and 6%) in the mixtures.

It was observed that with the increase in the cellulose nitrate concentration, the products become yellower in color.

PMMA-CN (12.2% N) Copolymers:

Transparent rods and sheets, free of air bubbles, were prepared successfully by bulk polymerization in the same way as the previously mentioned series; but the reaction time and temperature were reduced to 36 hr and 36°C, respectively, for the two cellulose nitrate concentrations (2 and 4%) in the mixtures.

The same phenomena of yellowing in color of the prepared copolymers was observed.

Solubility and Swelling of the Prepared Copolymers

Although solubility and swelling tests are very simple tests, they give good indications about the ultimate structure of the polymers, especially crosslinked ones.

The prepared PMMA-CN copolymers were irradiated for specific periods of up to 11.83 Mrad before testing.

With respect to the solubility test, the solvents used were benzene, chloroform, acetone, and butyl acetate. The obtained results showed that PMMA is completely soluble either before or after irradiation. The rate of solubility increases with the increase of irradiation dose.

On the other hand, PMMA-CN copolymers did not dissolve in any one of the mentioned solvents either before or after irradiation, but they swelled.

With respect to swelling tests, benzene was chosen because of its straightforward data. The obtained results are displayed graphically in Figures 2-4.

The obtained results show a sharp decrease in swelling with cellulose nitrate concentration in the copolymer, especially in unirradiated and lightly irradiated samples. This indicates the crosslinked structure of such copolymer, and the degree of crosslinking increases with cellulose nitrate concentration, nitrogen content of cellulose nitrate, and irradiation dose.

Percent Homopolymer

In these experiments, the samples were extracted in a Soxhlet extractor for 72 hr using a mixture of benzene and chloroform (1:1 by volume), then dried to constant weight. The obtained results are given in Table I.

Table I shows that MMA monomer copolymerizes readily with cellulose nitrate even at low concentrations of the latter. With respect to the irradiated copolymer samples, the percent homopolymer was zero for all cellulose nitrate concentrations and nitrogen contents.

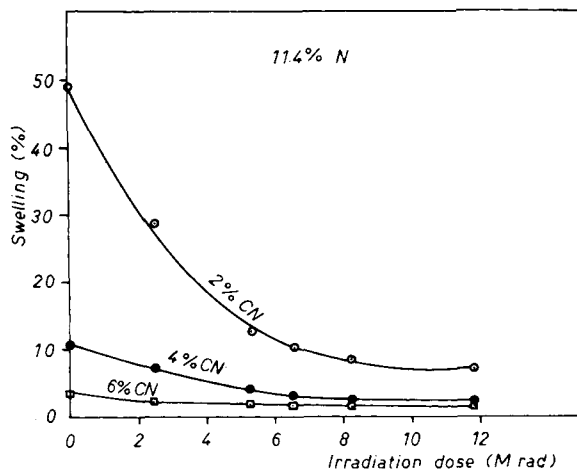


Fig. 2. Effect of irradiation on swelling of PMMA-CN copolymers.

TABLE I
Percent Homopolymer in PMMA+CN Copolymer

| PMMA-CN (11.4% N) copolymers | | | PMMA-CN (12.2% N) copolymers | |
|------------------------------|-------|-------|------------------------------|-------|
| 2% CN | 4% CN | 6% CN | 2% CN | 4% CN |
| 0.5 | 0 | 0 | 0.03 | 0 |

CONCLUSIONS

- (1) Suspension polymerization did not succeed in preparing PMMA-CN copolymers, especially when cellulose nitrate of low nitrogen content was used.
- (2) Rods and sheets of PMMA-CN were successfully prepared by bulk polymerization in the same way as PMMA but at lower temperatures.
- (3) PMMA-CN polymers are absolutely insoluble in conventional solvents, indicating crosslinked structure.

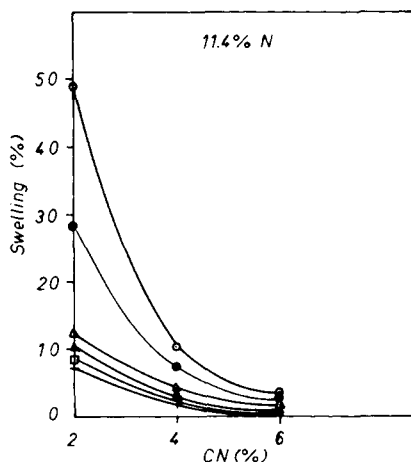


Fig. 3. Effect of CN on swelling of PMMA-CN copolymers: (O) 0.00 Mrad; (●) 2.50 Mrad; (▲) 5.26 Mrad; (▲) 6.57 Mrad; (□) 8.25 Mrad; (+) 11.83 Mrad.

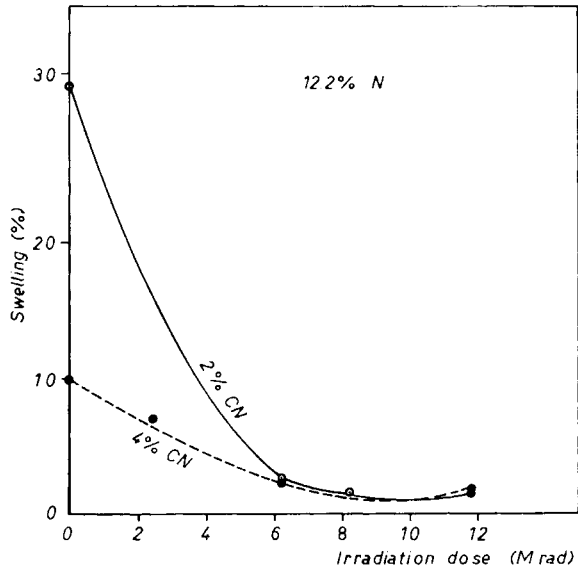


Fig. 4. Effect of irradiation on swelling of PMMA-CN copolymers.

(4) The degree of crosslinking goes hand in hand with cellulose nitrate concentration, nitrogen content, and irradiation doses of up to 8.25 Mrad.

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