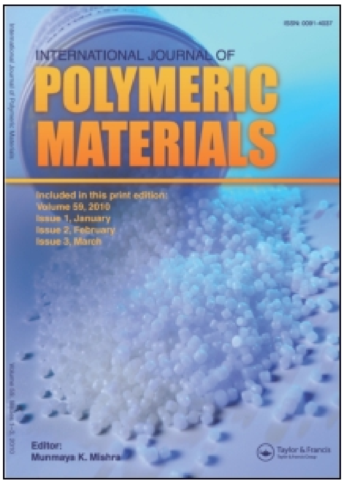

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Polymerization under Magnetic Field. Part 9. Polymerization of 2-Hydroxyethyl Methacrylate by Benzoyl Peroxide

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A systematic investigation of the influence of Magnetic Field on polymerization and copolymerization has been carried out on 2-hydroxyethyl methacrylate under UV-irradiation using benzoyl peroxide as initiator.

Keywords: Magnetic field; hydroxyl methacrylate; UV-irradiation; benzyl peroxide

INTRODUCTION

In the radical chain polymerization the three steps i.e., initiation, propagation and termination are associated with free radicals having unpaired electrons. These unpaired electrons have magnetic moments due to their spins, and, therefore, in a magnetic field (MF), the electron spin has a tendency to align itself in the direction of the applied field by making a precision motion around an axis. A strong influence of MF is, therefore, expected on the kinetics of radical polymerization which will be reflected in the yield, molecular weight and molecular weight distribution of the polymer.

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Besides, if the monomers having polar pendant groups are allowed to polymerize under MF, these pendant groups are expected to be oriented due to their diamagnetic anisotropy. Accordingly, more stereoregular and crystalline polymers may be expected to form under MF.

Moreover, if two monomers of different polarity are copolymerized under MF, the reactivity ratios of the comonomers, the copolymer composition and the monomer sequence in the copolymer chain are also expected to be altered. As a result, the polymer properties are supposed to be different under MF.

With this background we have started a program for systematic investigation on the influence of MF on polymerization/copolymerization, and observed that many of our above expectations proved to be true [1–6]. In this paper we wish to report the results on the polymerization of 2-hydroxyethyl methacrylate (HEMA) under UV-irradiation using benzoyl peroxide (BPO) as initiator at room temperature under MF.

MATERIALS AND METHODS

HEMA (Burgoyne, India) was purified as per the standard procedure and stored in a refrigerator at $\simeq 5^\circ$C.

BPO (Fluka, Switzerland) was recrystallized twice from cold chloroform solution, dried in a vacuum desiccator and stored in the dark at $\simeq 5^\circ$C in a refrigerator.

All other reagents are of analytical grade and used as received.

MAGNETIC FIELD

The polymerizations were conducted in the space between two adjustable poles of an electromagnet (Model EM 150, Control Systems & Devices, India) with a power supply. The strength of the magnetic field can be altered by adjusting the distance between two poles and the voltage of the power supply of the electromagnet. The MF strength was measured by a Gussmeter (Control Systems & Devices, India).

POLYMERIZATION

Stock solutions of HEMA with appropriate amounts of BPO were prepared. 2 ml of the stock solution and 10 ml water were taken in a quartz tube and the mixture was flashed with nitrogen to remove oxygen and the tube was closed by a rubber septum. It was then placed between the two poles of the electromagnet and was irradiated with a 400 W high pressure Hg-lamp (Philips India) placed at a distance of 32 cm away from the reaction tube. The polymer, poly (2-hydroxyethyl methacrylate) (PHEMA), was precipitated in a water-diethyl ether (50/50 v/v) mixture, filtered, dried at 50°C under vacuum and weighed till constant weight.

X-RAY DIFFRACTOMETRY

Wide angle X-ray diffractographs for the powder PHEMA samples were recorded with a Philips PW 1840 X-ray diffractometer using the Ni-filtered CuK$_\alpha$ ($\lambda = 1.5418$ Å) radiation at 40 kV-20 mA and a scanning speed of 1.2°/min.

RESULTS AND DISCUSSION

The effect of MF on the polymerization of HEMA using BPO as initiator is shown in Table I. The polymer yield obtained under MF is higher than that obtained without MF. The effect of MF on polymer yield may be defined as:

$$\phi_y = [\{\%\ \text{Yield (H)} - \%\ \text{Yield (O)}\} / \%\ \text{Yield (O)}] \times 100\% \qquad (1)$$

TABLE I Polymerization of HEMA under Magnetic Field[a]

MF (KG)	*% Yield*	ϕ_y^b (%)
0	56.15	–
1.15	72.08	28.4
5.05	73.02	30.0

[a] Polymerization conditions: 2 ml HEMA, 0.5% (w/w) BPO and 10 ml distilled water, 400 W high pressure Hg-lamp; room temperature; time = 15 min irradiation and 15 min for post polymerization. [b] According to equation 1.

where (H) and (O) refer to polymerization under MF and without MF, respectively.

The polymer yield increases by 28.4% and 30.0% by the application of MF of 1.15 KG and 5.05 KG, respectively. This observation may be attributed to the Δg-mechanism [7] and the cage effect of radical generation from the BPO decomposition [6, 8].

The X-ray diffractographs of PHEMA prepared with and without application of MF are shown in Figure 1. All these polymers are amorphous in nature whether prepared under MF or not. The crystallinity of PHEMA is expected to increase in presence of MF due to its long polar side chain crystallization. However, no appreciable MF effect is observed on the crystallinity of PHEMA, possibly due to low strength of the magnetic field used in these experiments.

The polymerization of liquid crystalline (LC) vinyl monomers having mesomorphic side chains (groups) produced well-oriented polymers under MF [9–11]. The polymerization of such vinyl monomers as (4-n-hexyloxyphenyl)-4-acryloyloxy benzoate under MF results in a fully oriented polymer [9]. Perplies *et al.* [10] polymerized the similar type of LC vinyl monomer, p-(4-ethoxyphenyliminomethylidene)-p-ethoxy-aniline

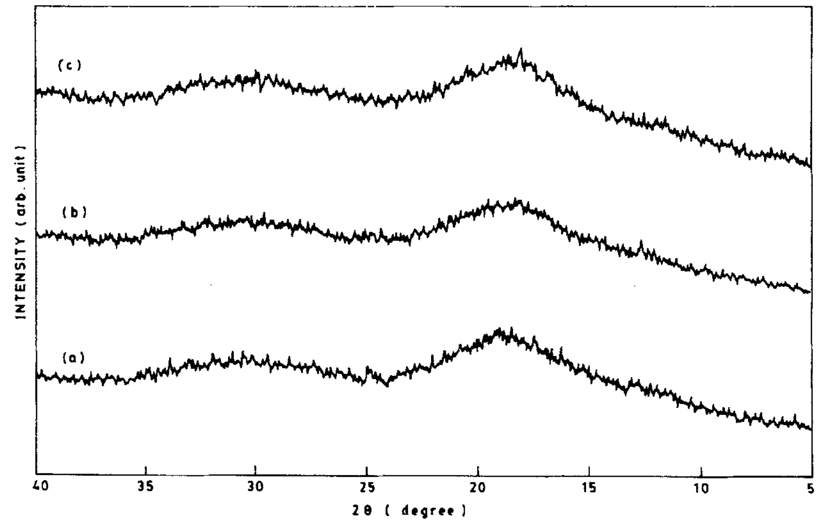

FIGURE 1 X-ray diffractograph of poly (2-hydroxyethyl methacrylate) prepared under magnetic field: (a) no magnetic field (0 KG); (b) 1.15 KG, and (c) 5.05 KG.

under MF of 70 KG and observed the higher degree of orientation of the polymer by X-ray diffraction. The copolymerization of two LC monomers, p-acryloyloxy benzylidene-p-cyanoaniline and di (N-p-acryloyloxy benzylidene)-p-diamino benzene under a MF of 8 KG produced highly oriented and crystalline polymer [11]. The reason of such observation was stated to be due to diamagnetic anisotropy in the LC phase. However, since HEMA does not possess the LC phase, the diamagnetic anisotropy of its side group is not sufficiently large to be oriented under MF of 5.05 KG. Therefore, no appreciable difference is observed in the X-ray diffractographs of PHEMA obtained with and without application of MF.

CONCLUSION

The MF increases the polymer yield when 2-hydroxyethyl methacrylate (HEMA) is polymerized under MF using benzoyl peroxide (BPO) as initiator. This is due to the Δ-g mechanism and the cage effect on the radical generation from the BPO decomposition. The influence of MF on the side chain crystallization is little observed by X-ray diffraction analysis of poly (2-hydroxyethyl methacrylate) (PHEMA) prepared under MF.

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