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Studies on Ultrasonic Degradation and Block Copolymerization of Hydroxyethylcellulose and Poly(ethylene Oxide)

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ABSTRACT

The ultrasonic degradation of hydroxyethylcellulose (HEC) and poly(ethylene oxide) (PEO) in aqueous solution, and the copolymerization of HEC with PEO were studied. The structure of the copolymer was identified by DTA, IR, MS, x-ray diffraction, and polarizing microscopy. The copolymer prepared is mainly block. The copolymer formed amounts to 55.07% by irradiating 0.5% HEC/PEO aqueous solution for a period of 10 min at 25°C and 18.2 kHz with 2.5 A input current on a reversed main circuit.

Poly(ethylene oxide) (PEO) and hydroxyethylcellulose (HEC) are two extensively used nonionic water-soluble polymers. They exhibit great stability in highly mineralized water. PEO is an extremely effective frictional drag reducer, but does not adhere to grit very well. HEC is the opposite. If a block or graft copolymer of PEO and HEC could be successfully prepared, a new polymer material that combines the merits of both PEO and HEC would be provided for exploration and exploitation of petroleum oil and natural gas fields.

In this paper the effects of ultrasonic intensity, solution concentra-

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tion, and reaction temperature on the ultrasonic degradation of HEC and PEO in aqueous solution are studied. The optimum condition for the ultrasonic copolymerization of an HEC/PEO mixture in aqueous solution as well as the yield, composition, and structure of the resultant copolymer are also preliminarily investigated.

EXPERIMENTAL

Materials

HEC: To a 1.5% filtrated aqueous solution of HEC add acetone in an amount three times that of the solution to precipitate HEC. Dissolve the precipitate and reprecipitate it once again, then vacuum dry it at 50-60°C to constant weight. The purified HEC possesses a molecular weight of $\overline{M}_n = 2.26 \times 10^5$, calculated according to $[\eta] = 4.70 \times 10^{-4}\ \overline{M}_n^{\ 0.80}$ (water, 25°C) [1].

PEO: To a 2% filtrated water/ethanol (1/1 by volume) solution of PEO add 1% glacial acetic acid. Then precipitate it by adding ether in an amount 1.2 times that of the solution. Dissolve the precipitate and reprecipitate it once again, then vacuum dry it at 50-60°C to constant weight. The purified PEO possesses a molecular weight of $\overline{M}_\eta = 2.48 \times 10^5$, calculated according to $[\eta] = 1.25 \times 10^{-4}\ \overline{M}_n^{\ 0.78}$ (water, 30°C) [2].

Ultrasonic Reactor

The reactor is the same as that reported in Ref. 3. The frequency adopted is 18.2 kHz. The amplitude probe is made of stainless steel (1Cr18Ni9Ti) with a diameter of 15 mm.

Ultrasonic Degradation

Add 1.0×10^{-3} mol/L hydroquinone (free radical terminator) to an aqueous solution of HEC (or PEO). Then carry out the degradation reaction under different conditions.

Ultrasonic Copolymerization of HEC/PEO in Aqueous Solution

Let a 0.5% aqueous solution of HEC/PEO (1/1 by weight) be ultrasonically irradiated for a certain period at 25 ± 1°C with a sonic intensity corresponding to 2.5 A input current on a reversed main circuit.

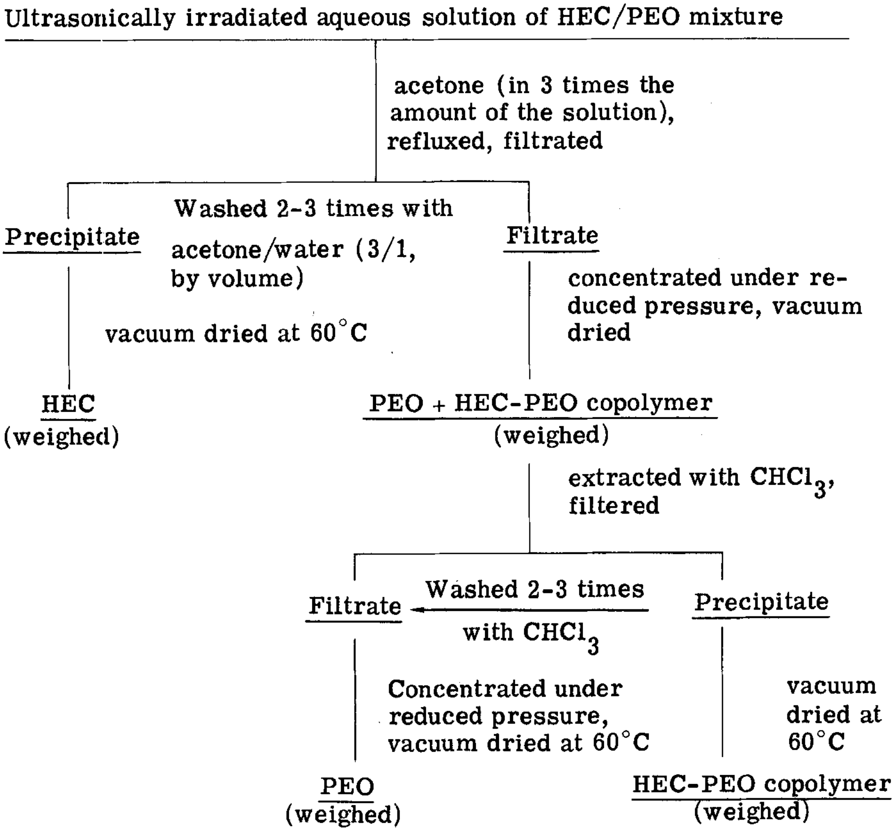


FIG. 1. Separation scheme of HEC, PEO, and HEC-PEO copolymer.

Then separate the copolymer formed according to the scheme shown in Fig. 1.

Identification of the Copolymer

The HEC-PEO copolymer is distinguished from a HEC/PEO mixture of the same composition by turbidity titration and DTA. The percent composition of the copolymer is determined by elementary analysis. The chemical and bulk structure of the copolymer are identified by IR and MS and by x-ray diffraction and polarizing microscopy, respectively.

RESULTS AND DISCUSSION

Ultrasonic Degradation of HEC and PEO

Figures 2-5 show the degradation curves of HEC and PEO of different concentrations at different sonic intensities. The degradation increases with an increase of sonic intensity and with a decrease of solution concentration. Both HEC and PEO degrade very rapidly in the early stages of irradiation. The curve gradually levels off to a limiting value with time.

During ultrasonic degradation, two macroradicals will be formed, each time by chain rupture. The chain scission number and the rate of radical formation can be calculated by the following equations [4]:

$$\nu = \overline{P}_o/\overline{P}_t - 1$$

$$dR^*/dt = 2cd\nu/dt \qquad (\mathrm{mol/L \cdot s})$$

where ν is the average chain scission number of each macromolecule at irradiation time t, c is the concentration of the polymer solution before degradation, and $\overline{P}_o$ and $\overline{P}_t$ are the number-average degrees of

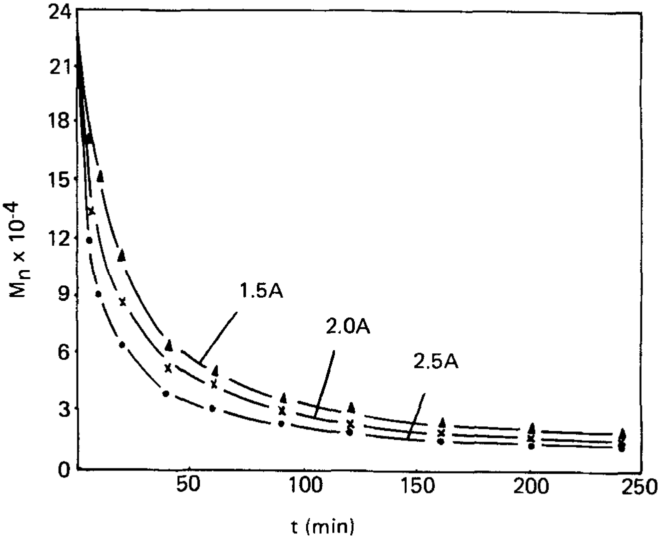


FIG. 2. Degradation of 0.5% HEC aqueous solution at different sonic intensities (25 ± 1°C).

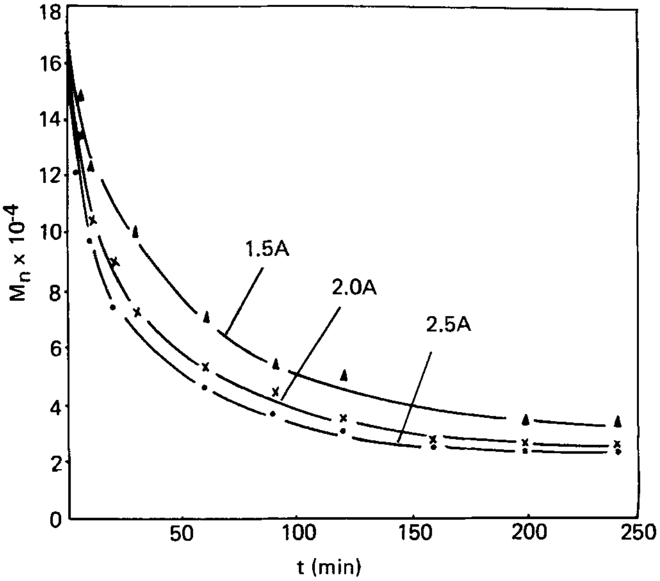


FIG. 3. Degradation of 0.5% PEO aqueous solution at different sonic intensities (25 ± 1°C).

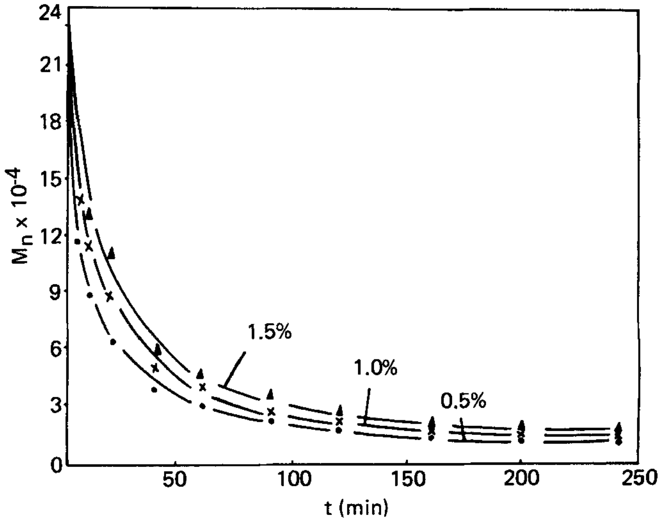


FIG. 4. Degradation of HEC in aqueous solution of different concentrations (sonic intensity: 2.5 A, 25 ± 1°C).

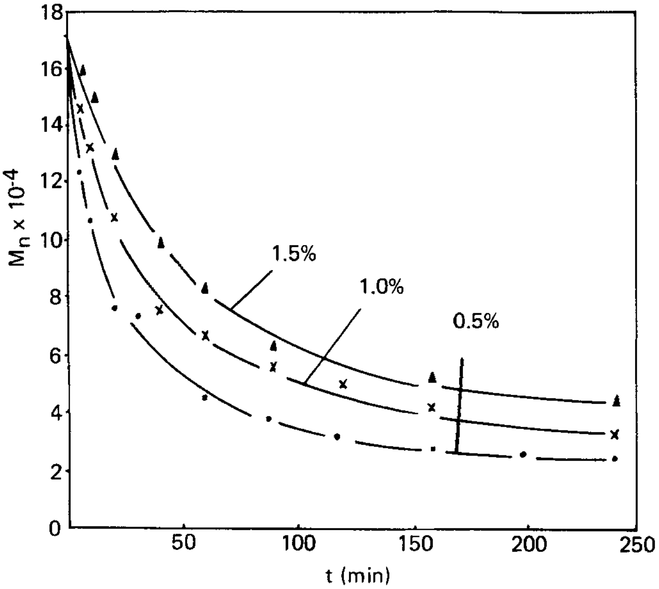


FIG. 5. Degradation of PEO in aqueous solution of different concentrations (sonic intensity: 2.5 A, 25 ± 1°C).

polymerization (D.P.) before irradiation and at irradiation time t, respectively. The ratio of viscosity average D.P. to number-average D.P. is given by [5]:

$$(\bar{P}_\eta/\bar{P}_n)^\alpha = \Gamma(3+\alpha)2^{(\alpha+1)}$$

where α is the exponent in the Mark-Houwink equation and Γ is the gamma function.

The data listed in Table 1 are the chain scission number and the macroradical formation rate of PEO and HEC during ultrasonic degradation in 0.5% aqueous solution. dR*/dt reaches a maximum when the irradiation time is 5 min, then decreases with irradiation time. The rigid chain is easier to degrade than the flexible one. The decrease in $\bar{M}_n$ of HEC amounts to 60.49% and that of PEO is 37.78% when they are irradiated for 10 min.

Ultrasonic Copolymerization of HEC and PEO

A higher yield will be reached if the copolymerization reaction is conducted at an early stage of irradiation where the rate of radical

TABLE 1. Chain Scission Number and Macroradical Formation Rate of HEC and PEO during Ultrasonic Irradiation ($\overline{M}_{no,HEC}$ = 2.26 × 10^5; $\overline{M}_{no,PEO}$ = 1.71 × 10^5; sonic intensity, 2.5 A, reaction temperature, 25 ± 1°C)

Irradiation time (min)	$\overline{M}_{nt} \times 10^{-4}$		$d\nu/dt \times 10^4$		$dR^*/dt \times 10^8$ mol/L·s	
	HEC	PEO	HEC	PEO	HEC	PEO
5	11.84	12.03	25.30	12.80	11.19	7.47
10	8.93	10.64	21.30	9.72	9.42	5.67
20	6.42	7.59	15.50	8.40	6.86	4.89
40	3.84		13.70	7.34	6.06	4.29
60	3.09	4.54	13.40	6.13	5.93	3.58
90	2.34	3.63	12.70	4.95	5.62	2.89
120	2.00	3.05	11.00	4.31	4.87	2.52
160	1.59	2.61	8.80	2.95	3.89	1.72
200	1.40	2.51	6.70	1.27	2.98	0.74
240	1.26	2.37	4.42	0.42	1.96	0.24

formation is relatively higher. The data listed in Table 2 show the dependence of the yield and the composition of the copolymer on irradiation time. The yield reaches to maximum with an irradiation period of 10 min. As the irradiation time increases, the copolymer yield decreases owing to a decrease in the rate of radical formation and chain scission of the copolymer.

Identification of the Block Copolymer

Elementary Analysis

The data listed in Table 3 are the hydrogen contents in 10 min irradiated samples as determined with a MOD-1106 elementary analyzer and the calculated value of PEO content in the copolymer. The latter is roughly close to the 10.84% (Table 2) obtained through the material balance.

Turbidity Titration

Figure 6 shows the turbidity curves of the HEC-PEO (91.19:8.81) copolymer and the HEC/PEO mixture of the same composition. A

TABLE 2. Dependence of the Yield and Composition of HEC-PEO Copolymer on Irradiation Time (HEC/PEO (1/1 by weight); concentration, 0.25%; 2.5 A; 25 ± 1°C)

Irradiation time (min)	Weight of sample (mg)				Yield (%)	PEO content in copolymer (%)
	Before irradiation, HEC + PEO	After irradiation				
		HEC	PEO	Copolymer		
5	166.6	5.6	75.0	85.6	51.38	9.48
10	171.6	0.6	76.8	94.5	55.07	10.84
20	166.1	16.9	70.8	73.3	44.13	8.61
30	166.4	29.5	75.6	59.3	35.64	6.73
40	165.6	37.6	79.0	49.6	29.95	5.70
60	159.6	51.5	79.1	30.4	19.05	2.63
90	165.0	61.2	79.7	23.4	14.18	2.55

TABLE 3. Hydrogen Content in HEC, PEO, and HEC-PEO Copolymer and PEO Content in Copolymer

Sample	H (%)	PEO in HEC-PEO (%)
HEC	6.66	
PEO	8.59	
HEC-PEO copolymer	6.83	8.81

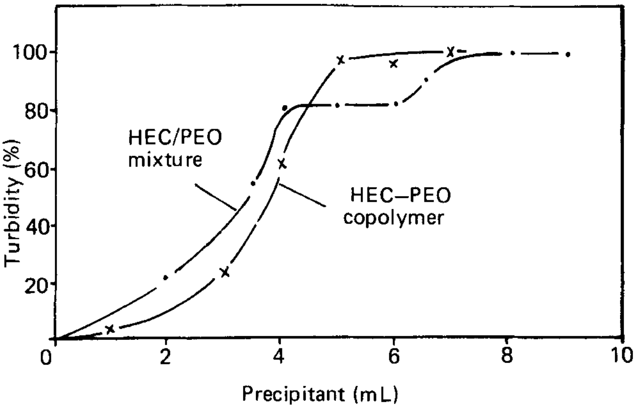


FIG. 6. Turbidity titration curves (wavelength 400 nm, determined 40 min after the addition of precipitant).

model 721 spectrophotometer was used with tannic acid and NaCl as precipitant [6]. A plateau occurs on the turbidity curve of the mixture when the amount of the precipitant added ranges from 4 to 6 mL, whereas the turbidity curve of the copolymer is continuous. This is because PEO and HEC each shows its own solution-precipitation behavior in the mixture.

DTA

Figure 7 is the DTA curves of the HEC-PEO (91.19:8.81) copolymer and the HEC/PEO mixture of the same composition, measured with a CDR-1 differential thermal analyzer. On Curve III of the mixture there is an obvious peak at 63°C, corresponding to the endothermal melting peak of PEO. At 321°C there is another small peak corresponding to the thermal decomposition temperature of HEC. On Curve IV of the copolymer, however, no peak appears at about 320°C, only the dehydration peak of HEC occurs at 57°C. This further suggests that HEC-PEO is a copolymer rather than a mixture of HEC and PEO.

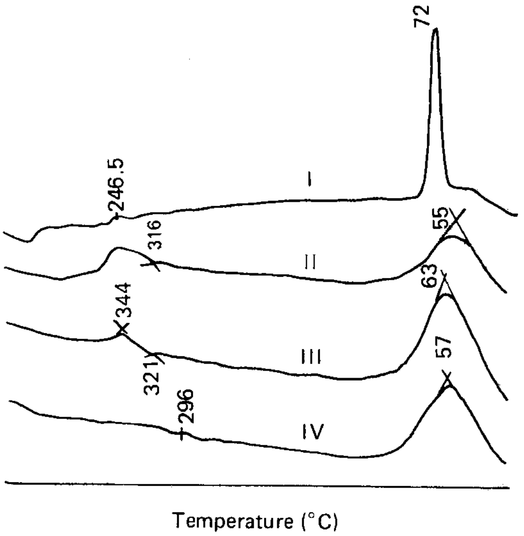
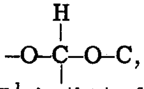


FIG. 7. DTA spectra (in N_2): I, PEO; II, HEC; III, HEC/PEO mixture; IV, HEC-PEO copolymer.

IR Analysis

Figure 8 shows the IR spectra of PEO, HEC, and HEC-PEO (91.19:8.81) copolymer obtained with a IR-450 IR spectrophotometer. The peaks at 885-890, 1000-124, and 1250-1429 cm^{-1} are the characteristic absorption peaks of $-CH_2OH$, $-C-O-C-$,  $-O-\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-O-C$, and $>$CHOH in HEC, respectively. The peak at 850 cm^{-1} is that of $-CH_2CH_2O-$ in PEO. The HEC-PEO copolymer possesses all the peaks possessed by the homopolymer HEC and PEO. By comparing the absorption intensity of $-CH_2OH$ in the copolymer and that in HEC, no obvious difference is found, thus the possibility of grafting at $-CH_2OH$ is excluded, otherwise the absorption intensity of the copolymer at 885-890 cm^{-1} would become noticeably weaker. Neither is there any obvious difference between the absorption intensity of $>$CHOH in the copolymer and that in HEC. All of these indicate that three –OH groups in the HEC chain unit have not been displaced and that the HEC-PEO copolymer obtained is mainly a block one.

Mass Spectrographic Analysis

Figures 9 and 10 are the mass spectra of HEC and HEC-PEO (91.19:8.81) copolymer measured with a MAT mass-spectrometer.

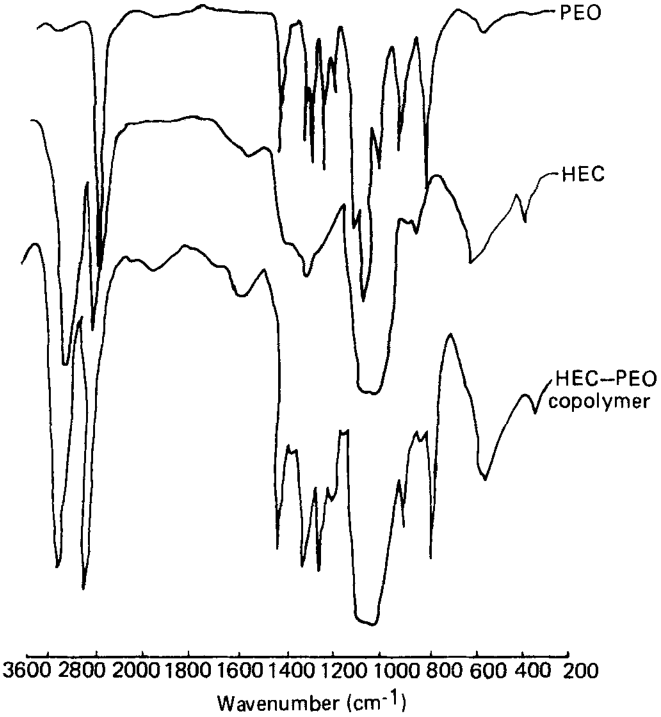


FIG. 8. IR spectra of PEO, HEC, and HEC-PEO copolymer.

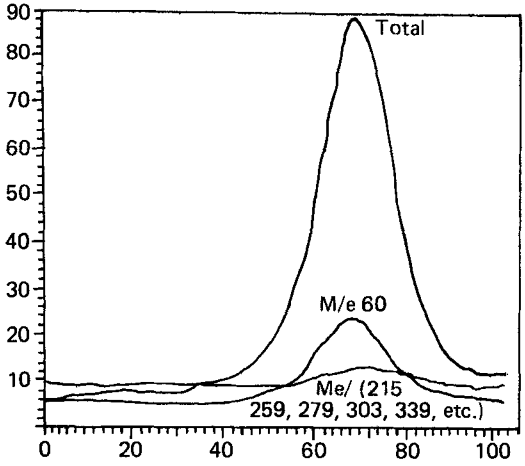


FIG. 9. Mass spectrum of HEC.

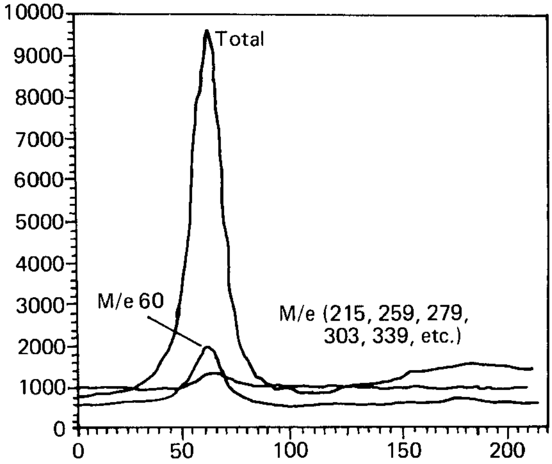


FIG. 10. Mass spectrum of HEC-PEO copolymer.

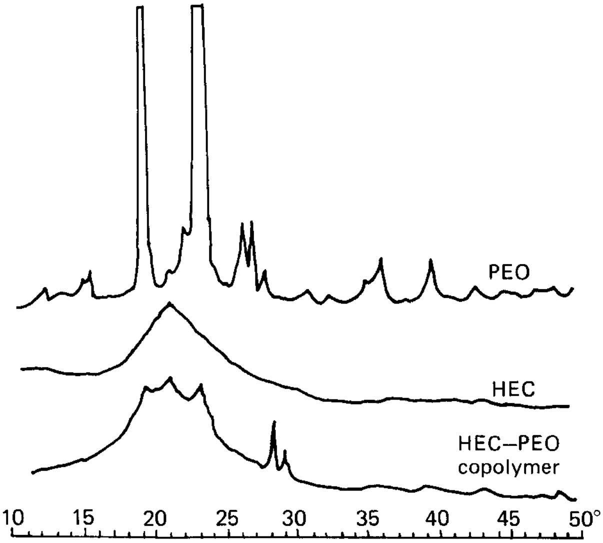
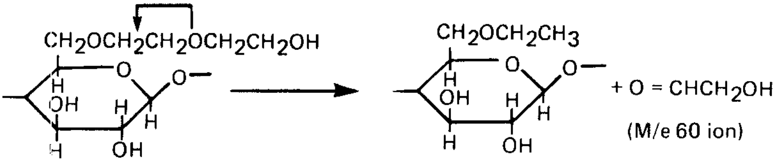


FIG. 11. X-ray diffraction spectra of HEC, PEO, and HEC-PEO copolymer (CuK_α, 35-40 kV, 20-30 mA, 8000 cps).

Because the M/e 60 ions are produced prior to ions of higher mass, it is believed that pyrolysis of HEC begins at the hydroxyethyl side group and then continues at the main chain. The M/e 60 ions are produced according to the following process:



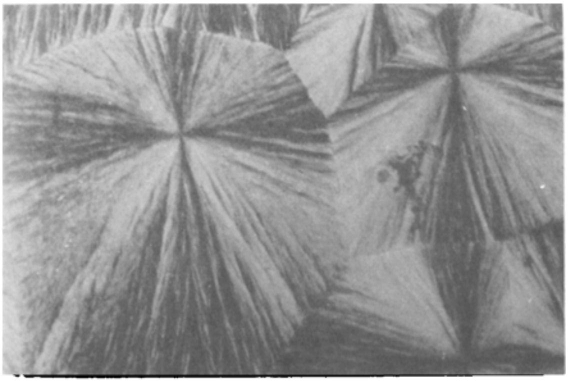
The ratio of the relative abundance of M/e 60 ions to that of the ions of higher mass (M/e 215, 259, 279, 303, 339, etc.) indicates the relative number of side groups in the HEC molecule. If copolymerization takes place at the side group, this ratio will decrease. The mass spectrum of HEC-PEO copolymer compared with that of HEC, however, does not show any decrease in this ratio. This also suggests that the copolymerization reaction occurs at the main chain rather than at the side chain of HEC.

X-Ray Diffraction

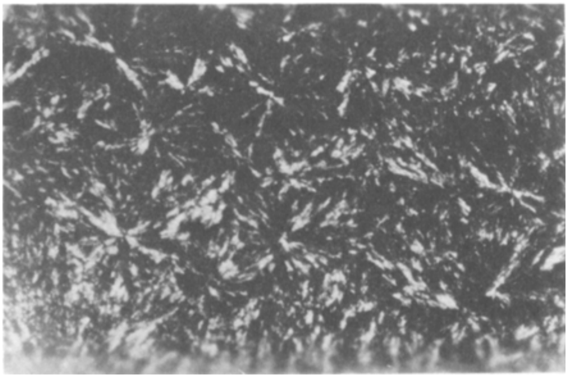
Figure 11 shows the x-ray diffraction spectra of HEC, PEO, and HEC-PEO block copolymer measured with a model 3015 x-ray diffraction-fluorescence spectrometer. The copolymer exhibits the characteristic peaks of PEO at a scanning angle (2θ) of 26-29°, indicating that both an oriented crystalline PEO region and an amorphous HEC region exist in the structure of the copolymer.

Polarizing Microscopy

Figure 12 is photographs of PEO and HEC-PEO block copolymer taken by a Row polarizing microscope at the cross position (extinction) of two Nicol prisms. It shows that the copolymer is amorphous, with some crystalline chain bundle in it. The dimension of the PEO spherulite is above 250 μm, while that in the copolymer is only about 80 μm.



PEO



HEC—PEO copolymer

FIG. 12. Polarizing microscopic photographs of PEO and HEC-PEO copolymer (×70).

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