

Preparation of Electrorheological Active Ionomers from Poly(2-hydroxyethyl methacrylate)-*co*-Poly(4-vinyl pyridine)

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ABSTRACT: In this study, synthesis, characterization, partial hydrolysis, and salt formation of poly(2-hydroxyethyl methacrylate)-*co*-poly(4-vinyl pyridine), (poly(HEMA)-*co*-poly(4-VP)) copolymers were investigated. The copolymers were synthesized by free radical polymerization using K₂S₂O₈ as an initiator. By varying the monomer/initiator ratio, chain lengths of the copolymers were changed. The copolymers were characterized by gel permeation chromatography (GPC), viscosity measurements, ¹H and ¹³C NMR and FTIR

spectroscopies, elemental analysis, and end group analysis methods. The copolymers were partially hydrolyzed by *p*-toluene sulfonic acid monohydrate (PTSA·H₂O) and washed with LiOH_(aq) solution to prepare electrorheological (ER) active ionomers, poly(Li-HEMA)-*co*-poly(4-VP). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3540–3548, 2006

Key words: poly(2-hydroxyethyl methacrylate)-*co*-poly(4-vinyl pyridine); synthesis; partial hydrolysis; ionomers

INTRODUCTION

Over the past two decades, hydrophilically modified polymers have attracted increasing interest owing to their practical and fundamental importance.¹ This system usually consists of a major part of hydrophilic backbone and a small proportion of hydrophilic groups. In this kind of polymer, intermolecular aggregates prevail over intramolecular ones, and clusters of hydrophilic domains are formed.² This leads to a transitional network structure that induces a substantial increase in solution viscosity. It is speculated that these dynamic junctions are disrupted upon high shear stress but will reform when the force ceases. Such salient macroscopical rheological features, as well as strong viscosifying ability, enable the attraction of hydrophilically modified polymers to various industrial uses, where the control of fluid rheology is required, for example, coatings, paints, cosmetics, drilling fluid, petroleum recovery, and foods. In the concentrated domain, physically linked viscoelastic gel can be obtained.³ This renders possibilities for appli-

cations in drug release and control, agricultural agents, adsorbents, or separation processes.

The understanding of the relationship between the molecular structure and final polymer properties represent another key aspect. A typical example is how the architectural parameters, such as the molecular mass of the polymer, the nature and level of the hydrophilicity, or the relative placement of the nonpolar groups along the polymer skeleton influence the rheological properties of the final solution.

It is believed that hydrophilically modified polymers can overcome the deficiencies of their unmodified analogues, namely, polyacrylate or partially hydrolyzed polyacrylate,⁴ block-copolymers of isoprene and tertiary butyl acrylate,⁵ which are sensitive to mechanical degradation, the presence of electrolytes, and high temperature.

As has been shown,⁶ the aggregation efficiency and thus the subsequent rheological properties of hydrophilically modified polymers rely strongly on their structural characteristics, notably on the content and the nature of hydrophiles and their distribution along the polymer chain. Other architectural parameters such as molecular mass and the properties of hydrophilic back-bone may play important roles as well. Synthetic processes can tune some of these variables; for instance, hydrophilic distributions and molecular mass.

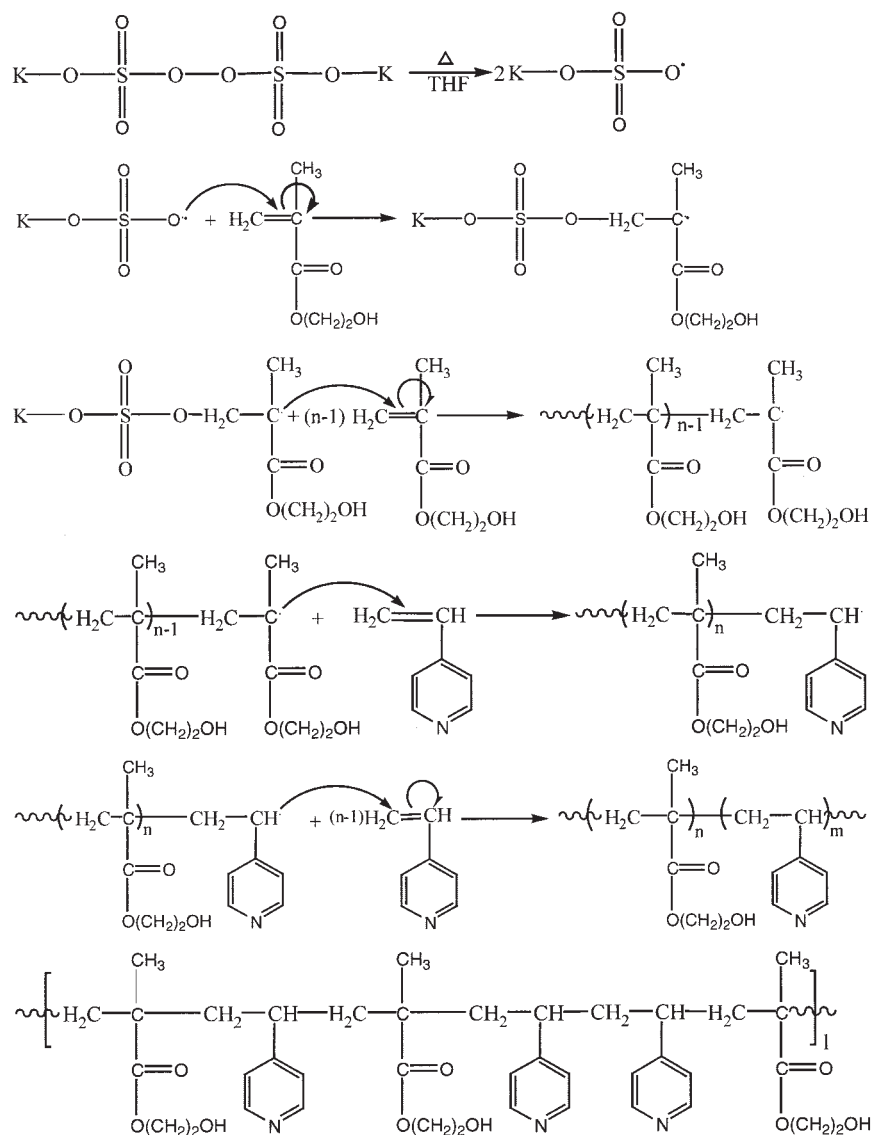
The polymers having the ionic groups are called ionomers. They have a relatively small number of ionic groups (up to 10–15 mol %) distributed usually along nonionic organic back-bone chains. Because of

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Scheme 1 The reaction mechanism of the free radical initiated copolymerization of HEMA and 4-VP.

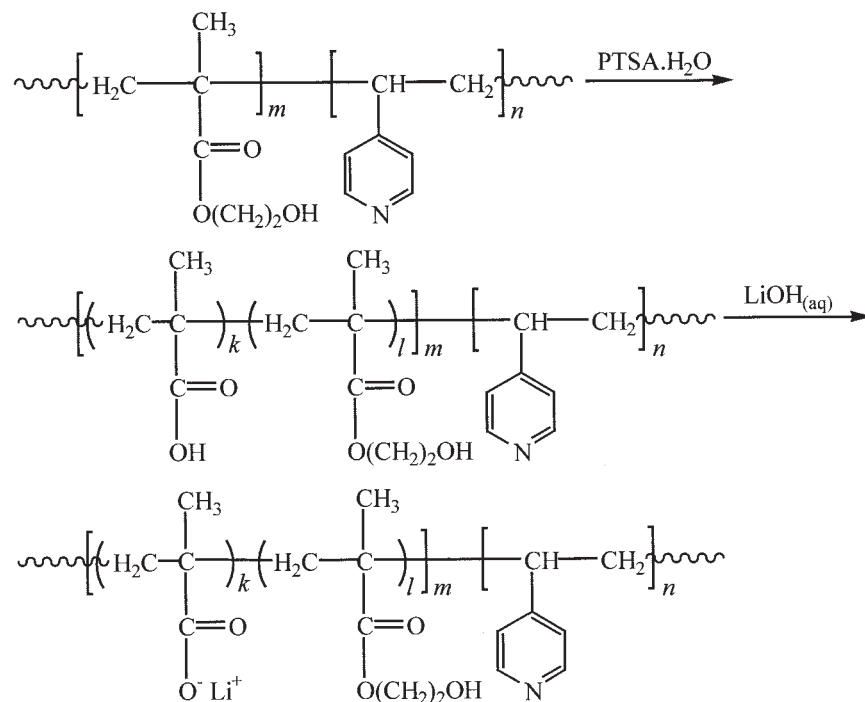
the low dielectric constant of the medium in which ionic groups are embedded, ionic groups tend to form ion pairs that further coalesce (due to the attraction between ion pairs) to create larger ionic aggregates. Such interactions include hydrogen bonding, ion–dipole interactions, acid–base interactions or transition metal complexation. Often, the extent of interaction can be controlled by the choice of the ionic group and/or the counter-ion, which provides considerable control of the morphology and final properties of the polymer.

Ion-containing polymers provide means of modifying various properties by controlling molecular structure through the utilization of ionic interactions. Ionomers rich in polar groups (copolymers containing hydrophilic and hydrophobic chains) can fulfill the criteria for the self-assembly formation.⁷ The reported phenomenon of surface micelle formation⁸ has been

found to be very general for these materials. Different morphologies arise depending on the diblock composition. As the relative ionic block length is decreased, different morphologies are observed.⁹

In the past, ion-containing polymers have been typically synthesized in our laboratory either by direct ionic polymerization^{10,11} or by free radical polymerization^{12–14} techniques with various vinyl comonomers, precursor to electrorheological (ER) studies.

In the present study, we detail the synthesis procedure of poly(2-hydroxyethyl methacrylate)-*co*-poly(4-vinyl pyridine) (poly(HEMA)-*co*-poly(4-VP)), its partial hydrolysis, ionomer preparation, [poly(HEMA-Li)-*co*-poly(4-VP)], and their structural elucidation. For this purpose, an attempt has been made to prepare high molecular mass copolymers and partially hydrolyze one of the blocks. Starting with 2-hydroxyethyl methacrylate (HEMA), a series of second block, 4-vi-



Scheme 2 Partial hydrolysis and salt formation reaction mechanism of poly(HEMA)-*co*-poly(4-VP).

nyl pyridine (4-VP), with different chain lengths was incorporated. Then, the acrylate units of the copolymers were partially hydrolyzed to obtain both with hydrophilic groups and charged units. To form ER active materials from copolymers of HEMA and 4-VP, poly(HEMA) units need to be partially hydrolyzed (i.e., 10%) to carboxylic acid units and converted to lithium salts. ER behaviors of these ionomers will appear in the following publication.

EXPERIMENTAL

Materials

Solvent

Tetrahydrofuran (THF) (Aldrich, Germany) purification was performed in vacuum.

Monomers

HEMA (Aldrich, Germany) and 4-VP (Aldrich, Germany) were stored below 0°C. The monomers were purified by vacuum distillation before being transferred into the reaction vessel by a drop funnel under a dry N_{2(g)} atmosphere.

Initiator

Potassium persulfate (K₂S₂O₈) (Aldrich, Germany) was dried in a vacuum oven at 70°C for at least 2 days, and used as received.

All other chemicals (Aldrich analar grade) were used as received.

Polymerization

HEMA, 4-VP, and K₂S₂O₈ were dissolved in THF at different compositions by keeping the mole number of one of the monomers constant, and changing the other and vice versa. K₂S₂O₈ at a concentration of 1.0% of the total mass of the polymerization mixture was used as a free radical polymerization initiator. All the reactions were carried out under dry N_{2(g)} atmosphere. All the glassware and transfer needles were dried by storing in an oven overnight at 140°C before use.

Polymerization was carried out in a three-necked flask equipped with a magnetic stirrer and a reflux condenser. Copolymers were prepared by free radical polymerization using THF as a solvent and K₂S₂O₈ as an initiator. K₂S₂O₈ (3.7×10^{-4} mol) was dissolved in 50 mL of anhydrous THF at 60°C, and then HEMA (with 6 different compositions: 10, 10, 10, 15, 20, and 25 mL) was added dropwise into the solution. The reaction mixture was stirred at 60°C for 2 h. Subsequently, 4-VP (with 6 different compositions 15, 20, 25, 10, 10, and 10 mL) was added dropwise into the living solution of homo poly(HEMA), and the reaction was allowed to proceed at 60°C for further 24 h. Then, each viscous solution of the copolymer was poured from the polymerization vessel into a beaker. Cooled *n*-hexane was slowly added onto this solution to precip-

TABLE I
Preparation Conditions of the Copolymers (COP1–COP6)

Copolymer	Monomer-1	Monomer-2	Volume-1 (mL)	Volume-2 (mL)	[1] + [2] (mol/L)
COP1	HEMA	4-VP	10	15	2.2
COP2	HEMA	4-VP	10	20	2.6
COP3	HEMA	4-VP	10	25	2.7
COP4	HEMA	4-VP	15	10	2.1
COP5	HEMA	4-VP	20	10	2.5
COP6	FIEMA	4-VP	25	10	2.9

[1] + [2]/[K₂S₂O₈] = 100; $T = (60.0 \pm 1.0)^\circ\text{C}$; $t = 24$ h; solvent = THF; non-solvent = *n*-hexane.

itate the copolymers separately. The precipitates were recovered and washed with methanol several times to remove any homopolymers and unreacted monomers present. The resulting copolymers were dried in a vacuum oven at 50°C for 2 days.

Copolymers have been coded with letters COP1–COP6 according to their synthesis order. When the acid units were converted to a lithium salt, letters “Li” suffixed the original coding.

Changing the molar ratio of comonomers, copolymers of differing compositions were produced with high yields (>92%), and different molecular masses obtained by varying the comonomer/initiator ratio. In all the copolymerization reactions carried out, homo poly(HEMA) was polymerized first, followed by the addition of the second monomer, 4-VP, onto this polymerizing homo poly(HEMA) solution. The reaction

mechanism of the copolymer formation is described in Scheme 1.

Characterization of the copolymers

FTIR spectra of the copolymers were recorded on a Mattson Model 1000 FTIR spectrometer as KBr discs.

Elemental analysis (LECO’s CHN-900, USA) was performed by microanalytical laboratory of Turkish Scientific and Technical Research Council (TUBITAK), and the results were used as a check for purity of the copolymers, the degree of hydrolysis, and percentage conversion to the Li salt.

At TUBITAK research laboratory, ¹H and ¹³C NMR spectra were recorded in dimethyl sulfoxide (DMSO-*d*₆) at a concentration of 0.2 g/cm³ at room temperature in 5-mm glass tubes, using a 400 and 100 MHz

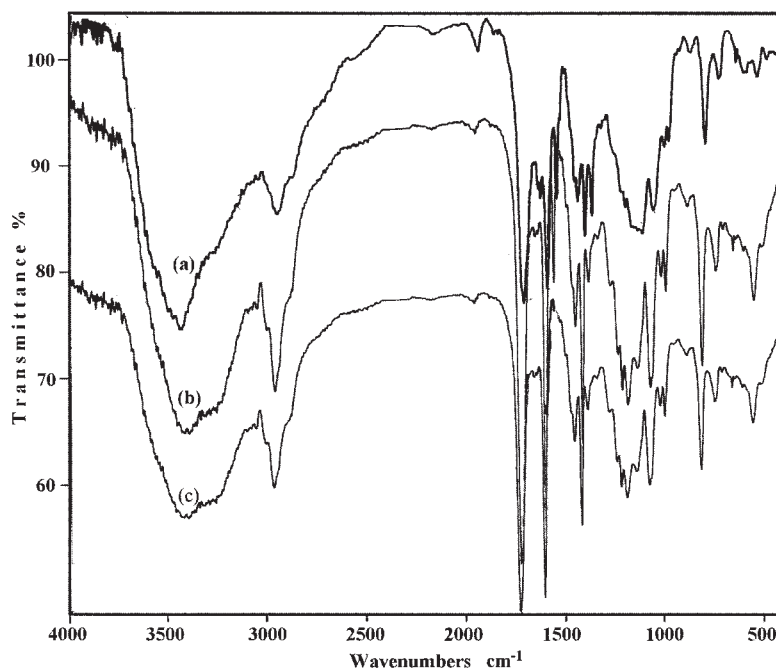


Figure 1 FTIR spectra of poly(HEMA)-co-poly(4-VP), (COP6): (a) before hydrolysis, (b) after hydrolysis, and (c) after converting to Li-salt.

TABLE II
FTIR Spectra Results of Poly(HEMA)-*co*-poly(4-VP)

Assignment	Wave numbers (cm ⁻¹)					
	COP 1	COP 2	COP 3	COP 4	COP 5	COP 6
—O—H	3425	3430	3430	3430	3430	3425
C—H (aromatic)	3040	3040	3040	3040	3040	3040
C—H	2845	2840	2845	2840	2845	2845
—C=O	1715	1720	1720	1715	1720	1720
—C=N	1580	1580	1580	1580	1570	1570
—C—O	1100	1100	1090	1100	1090	1100

Bruker 400 DPX Avance Nuclear Magnetic Resonance Spectrometer (USA), respectively, with an internal deuterium lock.

Molecular masses of the poly(HEMA) units of the copolymers were determined by end group analysis. For this, the copolymers were dissolved in KOH_(aq) solution, and titrated with standard 1.0M HCl_(aq) solution. The relationship used is given in eq. (1):

$$\text{Ester number} = \frac{M_{\text{KOH}}[V_1M_{1(\text{KOH})} - V_2M_{2(\text{HCl})}]}{m_{\text{copolymer}}} \quad (1)$$

The ester numbers obtained from eq. (1) for COP1–COP6 are multiplied by the molar mass of HEMA, and the number average molar masses of poly(HEMA) units were calculated.

Intrinsic viscosity, $[\eta]$, measurements of the copolymers were made in *n*-butanol using a Ubbelohde capillary flow viscometer, mounted in a water bath maintained at (25.00 ± 0.01)°C.

Gel permeation chromatography (GPC) was carried out at 25°C with THF as a solvent at a flow rate of 1 cm³/min using four μ -styragel columns (nominal pore sizes: 10⁶, 10⁴, 10³, and 500 Å) and a Waters 401 differential refractometer detector (Waters, Milford,).

The current-potential measurements were performed on an ionomeric salt disc (20 mm long, 5 mm wide, and 1 mm thick) with a Keithley 220 programmable current source and a Keithley 199 digital multimeter (Ohio, USA) at an ambient temperature. The capacitance, *C*, of ER particles was measured with an HP 4192 A LF Impedance Analyzer (San Diego, CA) at frequency of 1.0 MHz at constant temperature (20 ± 0.1)°C.

Hydrolysis of the copolymers and ionomer formations

To form ER active materials from copolymers of HEMA and 4-VP, HEMA blocks need to be partially hydrolyzed to carboxylic acid units and converted to

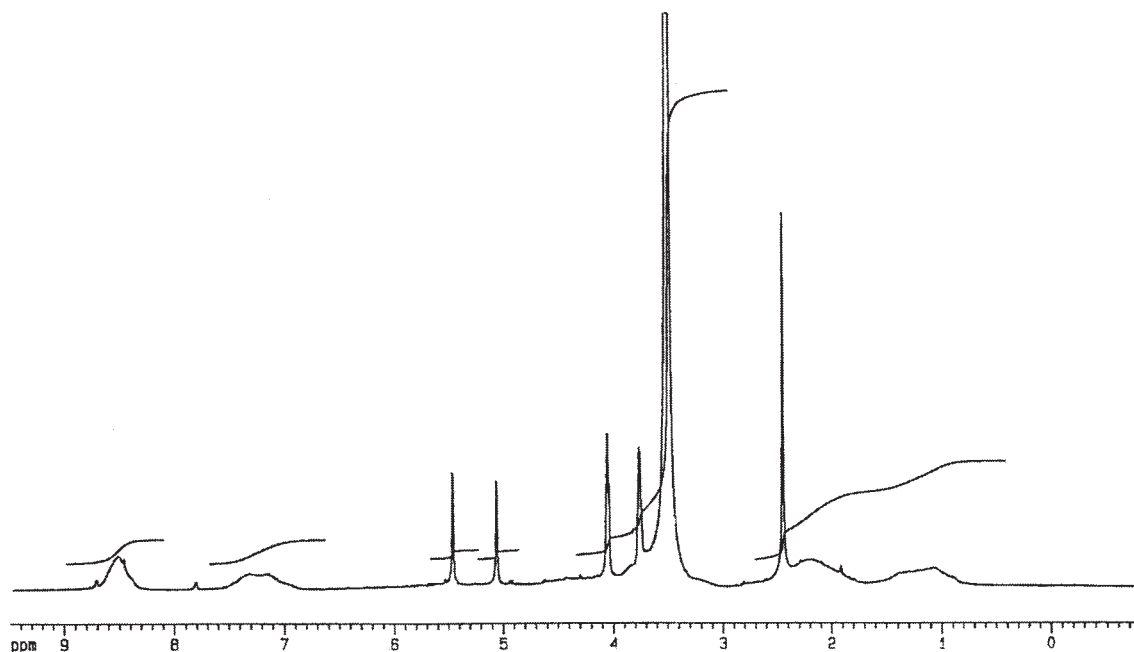


Figure 2 ¹H NMR spectrum obtained for COP6 in DMSO-*d*₆.

TABLE III
¹H NMR Spectra Results of Poly(HEMA)-*co*-poly(4-VP)

Assignment	Chemical shifts (δ , ppm)					
	COP 1	COP 2	COP 3	COP 4	COP 5	COP 6
—OH	5.05	5.07	5.05	5.11	5.03	5.06
—CH ₂ OH	3.72	3.72	3.73	3.72	3.72	3.72
—O—CH ₂ —	4.02	4.04	4.04	4.02	4.02	4.03
—CH ₂ —C—CH ₃	3.35–3.91	3.36–3.93	3.37–3.95	3.36–3.94	3.34–3.92	3.36–3.94
—CH ₃	1.30	1.31	1.30	1.29	1.29	1.29
—CH ₂ —CH—	2.16–2.35	2.17–2.36	2.18–2.36	2.18–2.38	2.16–2.36	2.17–2.37
CH ₂ —CH—	5.41	5.42	5.42	5.42	5.40	5.39
<i>o</i> —Ar—H	7.20	7.19	7.24	7.24	7.23	7.23
<i>m</i> —Ar—H	8.54	8.53	8.54	8.55	8.56	8.55

the Li salt. For this purpose, the copolymers were dissolved in *n*-butanol, and then *p*-toluene sulfonic acid monohydrate (PTSA·H₂O) was added to this solution (10% by mass of the copolymer) at 60°C and the solution was stirred for 30 min.¹⁵ The solution was then transferred to a separating funnel and washed with 100 cm³ LiOH_(aq) solution to remove residual PTSA·H₂O from the reaction medium. This organic phase was also washed with distilled water to remove any residual LiOH_(aq). The ionomer product, [poly-(HEMA-Li)-*co*-poly(4-VP)], was recovered from the solution and dried in a vacuum oven for at least 2 days at 15 mmHg. Then the moisture free ionomers were analyzed by FTIR and elemental analysis techniques. The reaction mechanism for the partial hydrolysis of the copolymers and the formation of ionomers are described in Scheme 2.

RESULTS AND DISCUSSION

Structural characterization of the copolymers

A range of poly(HEMA)-*co*-poly(4-VP) was synthesized successfully by free radical polymerization using K₂S₂O₈ as the initiator (Scheme 1). As seen from the Scheme 1, the free radical polymerization reaction mechanism produced random copolymers. The copolymerization reaction conditions are given in Table I.

The FTIR spectra obtained for unhydrolyzed, hydrolyzed, and Li-salt (ionomer) of poly(HEMA)-*co*-poly(4-VP) is shown in Figure 1. Before hydrolysis, the copolymer (COP6) shows a sharp stretching vibration of ester carbonyl bond of HEMA at 1720 cm⁻¹ [Fig. 1(a)]. After hydrolysis, appearance of the characteristic —OH band at 3400–3600 cm⁻¹ indicates that the partial hydrolysis was successful [Fig. 1(b)]. The FTIR spectrum of COP6-Li ionomer is also given in Figure 1(c). Since the copolymer was partially hydrolyzed and converted to Li-salt, as seen from the spectrum, the FTIR spectra of both hydrolyzed and Li-salt of the copolymer was almost identical. The FTIR spectra results obtained for the 6 unhydrolyzed copolymers (COP1–COP6) were essentially identical and given in Table II.

¹H NMR spectrum obtained just for COP6 is given in Figure 2. Also, the ¹H NMR results obtained for COP1–COP6 is summarized in Table III. As indicated in the table, all the expected distinctive chemical shifts are observed. The integration ratio of the main chain peaks to the peaks of methylene and methane protons is 4 : 3, also supporting the copolymerization of poly(4-VP). The chemical shift assignments were made from the off-resonance decoupled spectra of the copolymers.^{16,17}

The relationship used for the calculation of the conversion ratio of COP6 is given below. The same expression was used for the calculation of the conversion ratios of the other copolymers.

TABLE IV
 Composition Data of Poly(HEMA)-*co*-poly(4-VP) Calculated from ¹H NMR Spectra

Copolymer	Mole ratio (HEMA/4-VP)	Proton ratio (HEMA/4-VP)	Conversion ratio (HEMA/4-VP)
COP 1	0.59/1.00	1.82/1.00	1.01/1.00
COP 2	0.44/1.00	1.41/1.00	0.99/1.00
COP 3	0.35/1.00	0.81/1.00	0.99/1.00
COP 4	1.33/1.00	2.94/1.00	0.99/1.00
COP 5	1.77/1.00	3.19/1.00	0.99/1.00
COP 6	2.22/1.00	6.02/1.00	0.99/1.00

TABLE V
¹³C NMR Spectra Results of Poly(HEMA)-*co*-poly(4-VP)

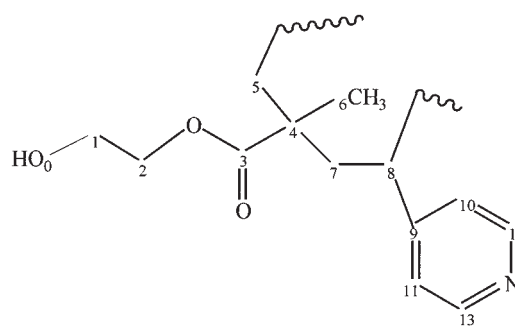
Carbon no.	Assignment	Chemical shifts (δ, ppm)					
		COP 1	COP 2	COP 3	COP 4	COP 5	COP 6
1	—CH ₂ OH	60	60	60	61	60	61
2	—O—CH ₂ —	65	66	66	66	65	66
3	—C=O	17	172	172	172	172	172
4	—CH ₂ —C—CH ₃	45	46	46	45	45	45
5	—CH ₂ —C—CH ₃	47	48	48	47	48	48
6	—CH ₃	24	24	24	23	24	24
7	—CH ₂ —CH—	42	43	44	43	42	43
8	—CH ₂ —CH—	55	56	55	55	56	55
9	Ar—C—	138	138	138	137	137	138
10,11	<i>o</i> —Ar—CH	121	121	122	121	121	122
12,13	<i>m</i> —Ar—CH—	146	148	147	146	146	147

$$\text{Conversion(\%)} = \left[\frac{I_{8.5} - I_{5.0}}{I_{8.5}} \right] \times 100 \quad (2)$$

Where $I_{8.5}$ and $I_{5.0}$ are the integration values of the peaks at $\delta = 8.5$ (belonging to the 4-VP proton) and $\delta = 5.0$ (belonging to the HEMA proton), respectively.

The chemical compositions of the copolymers were calculated by ¹H NMR method from the peak areas of the olefinic and aliphatic signals, and the results obtained are tabulated in Table IV.¹⁸

The ¹³C NMR spectra results of the copolymers are tabulated in Table V, according to the structure given below. The results confirm the copolymer structure, consisting of a poly(HEMA)-*co*-poly(4-VP) chains. The ¹³C NMR spectra of the copolymers showed the expected characteristic peaks of the monomeric units.



The estimation of four elements namely C, H, N, and O was done in the copolymers' compositions by the elemental analysis method. The expected and experimental results are shown in Table VI. For the calculation of expected percentage of C, H, N, and O, molecular masses of the copolymers obtained from GPC results were used.

TABLE VI
 Elemental Analysis Results and Compositions of Poly(HEMA)-*co*-poly(4-VP)

	C%	H%	O%	N%	Poly(HEMA)/poly(4-VP) (%)
COP1					
Expected	71.60	6.96	12.62	8.82	39/61
Experimental	64.18	6.85	12.10	6.58	
COP2					
Expected	72.09	6.94	11.67	9.09	35/65
Experimental	67.54	6.71	11.61	7.04	
COP3					
Expected	72.60	6.92	10.92	9.36	31/69
Experimental	67.45	6.32	10.82	7.15	
COP4					
Expected	71.10	7.70	15.20	7.00	35/65
Experimental	63.98	6.15	14.88	5.81	
COP5					
Expected	71.30	7.70	15.20	6.80	46/54
Experimental	61.85	6.60	15.10	5.44	
COP6					
Expected	71.40	7.70	18.90	6.70	47/53
Experimental	68.92	6.73	18.10	6.09	

TABLE VII
Molecular Mass Characteristics of Poly(HEMA)-*co*-poly(4-VP)

Copolymer	Ester number ^a	$\bar{M}_n \times 10^{-3}$ (g/mol) ^a	$\bar{M}_w \times 10^{-3}$ (g/mol) ^b	$\bar{M}_n \times 10^{-3}$ (g/mol) ^b	\bar{M}_w/\bar{M}_n^b	$[\eta]$ (dL/g)
COP1	352	37	113	94	1.5	1.72
COP2	268	35	171	100	1.7	1.75
COP3	246	32	164	102	1.6	1.81
COP4	346	44	202	126	1.6	2.06
COP5	442	57	197	123	1.6	2.11
COP6	498	64	190	135	1.4	2.17

^a Belong to poly(HEMA) units, obtained from end group analysis.

^b Belong to the copolymers, obtained from GPC.

By keeping the ratio of [HEMA] to [K₂S₂O₈] constant and varying [4-VP] concentration, COP1–COP3 were synthesized; and by keeping the ratio of [4-VP] to [K₂S₂O₈] constant and varying [HEMA] concentration, COP4–COP6 were synthesized. The compositions were estimated by calculating the nitrogen content of the copolymers. The nitrogen percentage increases from 6.58% (COP1) to 7.15% (COP3), with increase in 4-VP content (from 61 to 69%) in the copolymer compositions. On the other hand, the oxygen percentage increases from 14.88% (COP4) to 18.10% (COP6), with increase in HEMA content (from 35 to 47%).

Molecular masses of the copolymers

Molecular masses and molecular mass distributions of the six copolymers determined by end group analysis, viscosity measurements, and (GPC) methods are presented in Table VII.

The polydispersity indexes of the copolymers produced via radical combination and disproportionation are changes between 1.4 and 1.7. The values of \bar{M}_w/\bar{M}_n of these copolymers suggest that there is a strong tendency for chain termination by recombination.

Partial hydrolysis of the copolymers

Two criteria must be met for the polymer hydrolysis reactions to be effective. Firstly, the hydrolysis reagents must not affect the hydrocarbon block or result in any chain cleavage. Secondly, the extent of hydrolysis should be controlled. The reaction mechanism of hydrolysis and the formation of the Li salt of poly(HEMA)-*co*-poly(4-VP) copolymers are shown in Scheme 2.

It was shown by elemental analysis that the amount of Li in copolymers varies between 8.2–9.9% (Table VIII), which was aimed to be 10%. The reason for the target of 10% hydrolysis was to prepare ionomers from the copolymers and use them for the ER studies.

Solubility of the hydrolyzed copolymers and their Li salts was also investigated. It was observed that

these products are insoluble in most common solvents. Because of these solubility difficulties involved performing viscometry and GPC on the ionic systems was not possible.

Conductivity and dielectric analysis

The conductivities and dielectric constants of six ionomers were observed to increase linearly with the increasing ratio of poly(HEMA) to poly(4-VP) (Table IX). The maximum dielectric constant ($\epsilon = 1866$) and conductivity ($C = 7.28 \times 10^{-7}$ S/m) were measured at a frequency of 1.0 MHz, in the case of COP6-Li ionomer, which has 9.1% Li incorporated into the copolymer structure. On the other hand, COP6 also has the closest percentage ratio of poly(HEMA) (47%) to poly(4-VP) (53%). Such a dielectric constant is beneficial for use in ER fluids. These results are in the range of conductivity of ER particles.¹⁹ As expected, the driving force behind the ER activity of this ionomer/insulating oil system is the polarization of ionic particles suspended in a suspension.¹³ The dielectric constants were derived from the measured capacitance (C) according to the conventional relation:

$$\epsilon = Cd/\epsilon_0S \quad (3)$$

Where ϵ_0 is the dielectric constant of the vacuum, (i.e., 8.85×10^{-12} F/m),

TABLE VIII
Elemental Analysis Results of Poly(HEMA-Li)-*co*-poly(4-VP)

Ionomer	% Li (experimental) ^a
COP1-Li	9.9 ± 0.3
COP2-Li	9.8 ± 0.3
COP3-Li	8.7 ± 0.3
COP4-Li	8.2 ± 0.3
COP5-Li	9.4 ± 0.3
COP6-Li	9.1 ± 0.3

^a These were aimed to be 10%.

TABLE IX
Dielectrical Measurement Results of Poly(HEMA-Li)-*co*-poly(4-VP)

	COP1-Li	COP2-Li	COP3-Li	COP4-Li	COP5-Li	COP6-Li
Conductivity (S/m) $\times 10^7$	3.69	1.15	0.80	4.93	6.34	7.28
Relative dielectric constant	1512	1423	1340	1617	1714	1866

d is the distance of the gap between the electrodes, and

S is the contact area of the electrodes.

As suggested by Hao,¹⁹ the permittivity of an ER suspension should lie between 2 and 10,000. The permittivity of poly(Li-HEMA)-*co*-poly(4-VP) ionomers are well within the range expected for strong ER fluids.

CONCLUSIONS

1. Copolymers of 2-hydroxyethyl methacrylate and 4-vinyl pyridine were successfully prepared by free radical polymerization. Six copolymers were synthesized having different compositions and molecular masses.
2. Characterization results were confirmed for the presumed structure of poly(HEMA)-*co*-poly(4-VP) chains.
3. Depending on the initial ratio of HEMA and 4-VP, different copolymer structures could be obtained.
4. In addition to the interesting properties of the copolymers, these materials can also serve as precursors for subsequent polymer modification reactions. We have demonstrated a possible partial

hydrolysis route leading to ion containing electrorheological active polymers.

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