Synthesis of Block Copolymers via Redox Polymerization

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ABSTRACT: Polymerization and copolymerization of vinyl monomers such as acrylamide, acrylonitrile, vinyl acetate, and acrylic acid with a redox system of Ce(IV) and organic reducing agents containing hydroxy groups were studied. The reducing compounds were poly(ethylene glycol)s, halogen-containing polyols, and depolymerization products of poly(ethylene terephthalate). Copolymers of poly(ethylene glycol)s-b-polyacrylonitrile, poly(ethylene glycol)s-b-poly(acrylonitrile-co-vinyl acetate), poly(ethylene glycol)s-b-polyacrylamide, poly(ethylene glycol)s-b-poly(acrylamide-co-vinyl acetate), poly(1-chloromethyl ethylene glycol)-bpoly(acrylonitrile-co-vinyl acetate), and bis[poly-(ethylene glycol terephthalate)]-b-poly(acrylonitrile-co-vinyl acetate) were produced. The yield of acrylamide polymerization and the molecular weight of the copolymer increased considerably if about 4% vinyl acetate was added into the acrylamide monomer. However, the molecular weight of the copolymer was decreased when 4% vinyl acetate was added into the acrylonitrile monomer. Physical properties such as solubility, water absorption, resistance to UV light, and viscosities of the copolymers were studied and their possible uses are discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1385-1395, 1999

Key words: poly(ethylene glycol)s; acrylamide; acrylonitrile; block copolymers; redox polymerization

INTRODUCTION

Ce(IV) salts in aqueous acidic solution either by themselves¹ or in combination² with reducing agents are well-known initiators for vinyl polymerization. The polymerization mechanism involves complex formation between Ce(IV) salt and a reducing agent followed by the formation of free radicals that initiate the polymerization of vinyl monomers. The reducing agent may be alcohols,³ polyols,⁴ ketones,⁵ amino acids,⁶ carboxylic acids,⁷ hydroxy acids,⁷ poly(amino carboxylic acid)s,^{8,9} and amino methylene phosphonic acids.¹⁰ The resulting polymers were suggested to have chain ends of a corresponding reducing agent moiety. This method was used for the preparation of graft and block copolymers. Starch¹¹ and cellulose¹² were the most commonly used polymers for grafting. Recently, water-soluble cellulose derivatives such as methyl cellulose and methyl hydroxypropyl cellulose were used as reducing agents and their block/graft copolymers with polyacrylonitrile and polyacrylamide were produced.¹³ Block copolymers such as poly-(ethylene glycol)-b-polyacrylamide,¹³ polyacrylonitrile-b-poly(ethylene glycol) and polyacrylonitrile*b*-polyoxypropylene,¹⁴ ketonic resin-*b*-polyacrylonitrile,¹⁵ and ketonic resin-*b*-polystyrene¹⁵ were successfully prepared with such redox polymerization systems. Compared to other methods of block copolymerization, this type of redox polymerization possesses a number of advantages such as applicability of ambient temperature, using water as the media, and easy preparation of block containing both blocks of vinyl and condensation monomers.

Dedicated to the $225^{\rm th}$ anniversary of the Istanbul Technical University.

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The present work deals with the synthesis and characterization of a series of block copolymers containing blocks of condensation polymers such as poly(ethylene glycol)s, halogen-containing polyol, and depolymerization products of poly-(ethylene terephthalate), on the one hand, and blocks of vinyl polymers from such monomers as acrylamide, arylonitrile, vinylacetate, and acrylic acid, on the other hand. The block copolymers were obtained through redox polymerization of the monomers by using appropriate polymeric diols as reducing agents and Ce(IV) as the oxidant in an aqueous medium.

EXPERIMENTAL

Reagents

Poly(ethylene glycol) (PEG) with molecular weights of 200, 400, 600, 1500, and 4000 (Henkel, Düsseldorf, Germany) and halogenated polyether polyol Ixol B 251 with a molecular weight about 450 (Solvay, Bruxelles, Belgium) were used as received. Poly(ethylene terephthalate) (PET) with molecular weight of about 20,000 was the product of Sasa (Adana, Turkey). A stock solution of 0.1Mceric ammonium nitrate (Fluka, Buchs, Switzerland) in 1N HNO₃ was prepared and stored in a refrigerator. Polymerization grades of vinyl monomers, that is, acrylamide (AAm) (Fluka), acrylonitrile (AN, Fluka), vinyl acetate (VAc, Fluka) and acrylic acid (AA, Fluka) were used as received.

Depolymerization of PET¹⁶



A mixture of 0.88 mol PEG and 0.42 mol PET was heated to 230–240°C in the presence of titanium tetraisopropoxide for 5 h while formed ethylene glycol was collected into a Dean–Stark trap. The mixture was then cooled to room temperature and filtered. When diethylene glycol and PEG 200 were used for depolymerization, the depolymerization product (DPETDEG and DPETPEG200, respectively) was viscous. Depolymerization of PET with ethylene glycol was also carried out with an excess of ethylene glycol. After 5-h reaction time, the excess ethylene glycol was distilled off and collected into a Dean–Stark trap. The depolymerization product (DPETEG) appeared as solid white crystals. Hydroxyl values of depolymerized products were determined with acetic anhydride and found to be about the same as the theoretical values.

Synthesis of Block Copolymers

The synthesis of block copolymers was carried out in aqueous medium according to the previous article.¹³ A typical procedure is as follows:

Into a three-necked flask equipped with a dropping funnel and nitrogen inlet, 2 g PEG, 20 g vinyl monomers, and 100 mL water were charged. Then, a 25-mL Ce(IV) stock solution was added dropwise in 15 min in the dark under a N_2 atmosphere at 20°C while stirring the content of the flask with a magnetic stirrer. The vessel was then stoppered and the stirring was continued further for 2 h. The copolymers formed were recovered as follows:

- (a) The water-soluble copolymers were precipitated out by pouring their viscous aqueous solution into excess acetone. They were then filtered, washed with acetone several times, and finally dried under a vacuum.
- (b) The water-insoluble copolymers became precipitated during the polymerization. Some more water was added into the reaction flask to allow flocculation of the precipitate. The powdery copolymers were then filtered, washed several times with water and then with acetone, and finally dried under a vacuum. They were purified by reprecipitation in water from the DMF solution.

On carrying out similar experiments under comparable conditions, taking the monomers and Ce(IV) in the absence of the selected reducing agents, no polymer was formed in 4 h at 30°C in the dark, indicating that no homopolymerization of the vinyl monomers occurred during the block copolymer synthesis.

Characterization

Spectral Studies

FTIR spectroscopy was used to elucidate the structure of the copolymers using a Jasco FTIR-5300 spectrometer. The samples were made as pellets with KBr or as film prepared by solvent casting. ¹H-NMR and ¹³C-NMR spectra of the copolymers were recorded on a Bruker AC-200 spectrometer using DMSO- d_6 , and D₂O as the solvent containing TMS and DDS as an internal standard, respectively. The UV absorbances of the products in solution (DMF or water) were obtained using a Perkin–Elmer UV/vis spectrometer Lamda 2.

Molecular Weight Calculation from Viscosity

Molecular weights of copolymers were calculated from a single-point viscosity measurement at 25°C using an aqueous solution for poly(AAm) copolymers and a DMF solution for poly(AN) copolymers and making use of the following equations¹⁷⁻¹⁹:

$$ig|\etaig| = rac{\eta_{ ext{sp}}}{1+0.28 imes\eta_{ ext{sp}}}$$

for poly(AAm) copolymers:

$$|\eta| = 6.8 imes 10^{-4} imes M_n^{0.66}$$

for poly(AN) copolymers:

$$|\eta| = 2.33 imes 10^{-4} imes M_w^{0.75}$$

Molecular Weight Calculation from ¹H-NMR

The molecular weights of PEG-based poly(AAm) and poly(AN) copolymers were calculated from the ratio of the integration intensities of the signal due to methylene protons of vinyl monomers and the signals due to methylene protons of PEGs assuming no homopolymers were present in the copolymers. This ratio equals 2n/4m, with m the number of oxyethylene units of PEG and n the degree of polymerization of the vinyl monomer.

Rheological Properties

The rheological properties of the polymer solution in the appropriate solvent were measured using a Brookfield RVDV-II viscometer at different shear rates using a spindle no. 7 in a micro sample adaptor.

Weather Resistance

A Heraeus Suntest accelerated exposure machine with a 1.1 kW Xenon burner was used for an accelerated weathering test of the copolymers.

RESULTS AND DISCUSSION

The redox reaction between Ce(IV) and hydroxyl groups of the reducing polyols produces free rad-

icals that readily initiate polymerization of the vinyl monomers. The initial concentration of the monomers, PEG, and Ce(IV) and the molecular weight of the produced PEG-based block copolymer suggest that primary radicals formed on only one end of PEG on average was effective to initiate polymerization under the experimental conditions described in this work. The polymerization proceeds in accordance with Scheme 1.

Both mutual and oxidative terminations are possible and this results in a mixture of ABA- and AB-type block copolymers. However, polymer chains formed from primary diradicals of PEG results in BAB- and BABAB-type multiblock PEG-based copolymers. The extent of oxidative termination is dependent on the Ce(IV) concentration and the type of mutual termination (combination) is dependent on the type of monomer. AAm, AN, VAc, and AA were used as vinyl monomers and three different types of polyols were used as reducing agents, in order to produce block copolymers containing both condensation- and vinyl-type blocks. The block copolymers would contain at least one hydroxyl group that could be used as a reactive site to produce the derivatives of the copolymers. The presence of hydroxyl groups in this type of copolymer was proved by the reaction of hydroxyl groups with diisocyanate.14

Polyol–Poly(AAm) Copolymers

Water-soluble block copolymers produced from acrylamide and polyols were purified by dissolving in water and precipitating in acetone. This enables the unreacted polyols to be removed. Under similar experimental conditions, a poly(AAm) homopolymer was not formed if the temperature was below 40°C. The water-soluble copolymers so isolated contained neither the polyacrylamide homopolymer nor unreacted polyol. VAc was intentionally used in a small percentage as a comonomer in some experiments. The polymerization yields and molecular weights were rather low when AAm was homopolymerized by the polyol/Ce(IV) redox systems (Table I). Molecular weights of PEG-*b*poly(AAm) block copolymers

 $\begin{array}{c} \mathsf{HOCH}_2\mathsf{CH}_2\mathsf{O}(\mathsf{CH}_2\mathsf{CH}_2\mathsf{O}) \underset{m}{\overset{\mathsf{CH}_2\mathsf{CH}}{\overset{\mathsf{+}}{\underset{\mathsf{CONH}_2}}}{\mathsf{CONH}_2} \mathsf{CH}_2\mathsf{CH$

PEG-b-Poly(AAm)

I. Radical Generation and Chain Initiation

II.Propagation

III. Termination

a) Bimolecular Termination (combination)

$$\xrightarrow{\text{CH}_2\text{CH}_{\leftarrow}\text{CH}_2\text{CH}_{\rightarrow_n}\text{CH}_2\dot{\text{CH}} + \xrightarrow{\text{CH}_2\text{CH}_{\leftarrow}\text{CH}_2\text{CH}_{p}\text{CH}_2\dot{\text{CH}}_{p} \text{CH}_2\dot{\text{CH}}_{p} \text{CH}_{p} \text{CH}$$

b) Unimolecular Termination (oxidative termination by Ce⁺⁴)

$$\overset{\text{ch}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_1\text{CH}_2\text{CH} + \text{Ce}^{+4} \rightarrow \overset{\text{ch}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_1\text{CH}_2\text{CH}_1\text{CH}_2\text{CH} + \text{Ce}^{+3} + \text{H}^+ \\ \overset{\text{ch}_2\text{CH}$$

Scheme 1

were in the range of 10,000. Increasing the content of vinyl acetate as the comonomer resulted in a gradual increase in both the polymer yield and the molecular weight (Table I). Chain initiation by reaction of vinyl monomers with primary polyol-based free radicals leads to the formation of chain radicals and ultimately to block copolymers. The reactivities of the vinyl monomers and of the radicals derived from them will be important in determining the rate and the yield. The increase in the yield and the molecular weight on use of an increasing proportion of VAc as a comonomer along with AAm giving polyol-bpoly(AAm-co-VAc) may be related to the higher reactivity of VAc chain radicals produced in an increasing proportion in the system. Addition of 4% AAm or AA monomer instead of VAc had little effect on the polymerization yield (Table II).

PET was depolymerized with PEGs at 230°C for 5 h in order to obtain water-miscible and -soluble diesters of terephthalic acid. Diester (DPETEG) obtained from ethylene glycol and PET was not water soluble at room temperature. These depolymerized PET products were used as reducing agents and water-soluble block copolymers of DPETEG-bpoly(AAm-co-VAc), DPETDEG-b-poly(AAm-co-VAc), and DPETPEG200-b-Poly(AAm-co-VAc) were produced. Again, the addition of VAc into the AAm monomer resulted in a higher polymerization yield. Increasing the amount of VAc from 2 to 8%, resulted in the yield to increase from 15 to 70%. These depolymerized PET-based block copolymers were recovered easier than were PEG-based block copolymers when their water solutions were poured into acetone. This may be due to the lower water solubility of the terephthaloyl moiety of depolymerized PET-based water-soluble copolymers. When waterinsoluble DPETEG was used as a reductant, a mixture of water : acetone (3:7) was used as a solvent for the polymerization.

The FTIR spectra of purified water-soluble block copolymers of PEG-poly(AAm) [PEG-b-

Reducing Agent	Monomer Concentration AAm : VAc (mol/L)	Copolymer	Yield (%)	Molecular Weight
PEG200	2.4:0.00	PEG200-b-poly(AAm)	< 2	_
PEG200	2.4:0.1	PEG200- <i>b</i> -poly(AAm- <i>co</i> -VAc)	34	130,000
$\rm PEG400^{a}$	2.4:0.00	PEG400- <i>b</i> -poly(AAm)	15	7,200
PEG400	2.4:0.1	PEG400- <i>b</i> -poly(AAm- <i>co</i> -VAc)	65	97,500
PEG600	2.4:0.00	PEG600- <i>b</i> -poly(AAm)	4	
PEG600	2.4:0.1	PEG600- <i>b</i> -poly(AAm- <i>co</i> -VAc)	26	104,000
PEG1500	2.4:0.00	PEG1500-b-poly(AAm)	3	
PEG1500	2.4:0.05	PEG1500-b-poly(AAm-co-VAc)	8	44,000
PEG1500	2.4:0.1	PEG1500-b-poly(AAm-co-VAc)	18	160,000
PEG4000	2.4:0.00	PEG4000-b-poly(AAm)	< 2	
PEG4000	2.4:0.05	PEG4000-b-poly(AAm-co-VAc)	12	31,000
PEG4000	2.4:0.1	PEG4000-b-poly(AAm-co-VAc)	34	240,000
$DPETEG^{b}$	2.4:0.1	DPETEG-b-poly(AAm-co-VAc)	12	35,400
DPETDEG	2.4:0.1	DPETDEG-b-poly(AAm-co-VAc)	61	72,000
DPETPEG200	2.4:0.05	DPETPEG200- <i>b</i> -poly(AAm- <i>co</i> -VAc)	15	
DPETPEG200	1.2:0.1	DPETPEG200- <i>b</i> -poly(AAm- <i>co</i> -VAc)	70	260,000

Table I Aqueous Polymerization of AAm Using the Redox Pair of Polyol/Ce(IV)

Polymerization time = 2 h; temperature = 26°C; [Ce(IV)] = 13 mmol/L, [polyol] = 20 g/L.

^a Polymerization temperature = 32°C.

^b Polymerization solvent = acetone : water (3:7).

poly(AAm)] showed overlapping peaks of both poly(AAm) and polyol (Fig. 1). A broad peak due to both amid NH— and —OH stretching was observed at between 3400 and 3200 cm⁻¹. A sharp peak due to C—O stretching at 1660 cm⁻¹ and a weak peak due to C—O stretching at 1120 cm⁻¹ were observed. The FTIR spectra of the copolymer containing 4% AN comonomer PEG-*b*-poly(AAm*co*-AN) showed a small characteristic C=N stretching band at 2250 cm⁻¹.

Depolymerized PET-based water-soluble copolymers contained benzene rings which were easily detected by UV. The UV-vis spectra of the acrylamide copolymers were recorded in H_2O . In all cases, a strong absorbtion centered at about 210 nm was assigned to amide groups of the polymers. The copolymers, DPETEG-*b*-poly(AAm-*co*-VAc) and DPETPEG200-*b*-poly(AAm-*co*-VAc), showed additional maxima at about 278 nm due to the benzene ring. The UV-vis spectrum of homopoly-acrylamide did not contain any absorption at about 278 nm (Fig. 2).

The ¹H-NMR spectra of the copolymers are shown in Figure 3. The acrylamide methylene and methine groups appeared as a broad band at 1.75 and at 2.3 δ ppm, respectively. Poly(ether methylene) protons appeared at 3.75 δ ppm. The copolymers containing the depolymerized PET

 Table II
 Polymerization of AAm Containing a Small Amount of AN and AA

 with the Redox Pair of Polyol/Ce(IV)

Reducing Agent	Monomer Concer (mol/L)	ntration	Copolymer	Yield (%)
PEG4000	AAm : AN (2.4	: 0.16)	PEG4000- <i>b</i> -poly(AAm- <i>co</i> -AN)	4
PEG4000	AAm : AN (2.4	: 0.32)	PEG4000-b-poly(AAm-co-AN)	3
PEG200	AAm : AA (2.4	: 0.1)	PEG200-b-poly(AAm-co-AA)	3
PEG400	AAm : AA (2.4	: 0.1)	PEG400-b-poly(AAm-co-AA)	8
PEG600	AAm : AA (2.4	: 0.1)	PEG600-b-poly(AAm-co-AA)	7
PEG1500	AAm : AA (2.4	: 0.1)	PEG1500-b-poly(AAm-co-AA)	3
PEG4000	AAm : AA (2.4	: 0.1)	PEG4000-b-poly(AAm-co-AA)	4

Polymerization time = 2 h; [polyol] = 20 g/L, temperature = 26°C; [Ce(IV)] = 13 mmol/L.



Figure 1 FTIR absorbtion spectra of the water-soluble copolymers on KBr pellets.

moiety such as DPETPEG200-*b*-poly(AAm-*co*-VAc) displayed a very small additional integration intensity for the band at about 8.7 δ ppm that



Figure 2 UV-vis absorbtion spectra of the water-soluble copolymers in H_2O .



Figure 3 1 H-NMR absorbtion spectra of the watersoluble copolymers in D_2O .

represents the benzene ring of terephthaloyl group. The four equivalent aromatic protons were deshielded by the adjacent ester carbonyl groups and appeared at lower field, near 8.7 δ ppm.

The molecular weight of PEG-based copolymers were calculated from ¹H-NMR signal ratios. The integration intensities of the signals of PEG methylene protons (3.75 δ ppm) and acrylamide methylene protons (1.75 δ ppm) were used for the molecular weight calculations. The values were in good agreement with the molecular weight determined with the viscosity method (Table III).

Polyol-b-poly(AN) Polymers

The block copolymers of polyol and poly(AN) had solubility properties similar to those of poly(AN). The copolymers became precipitated during the polymerization. The copolymers were freed of residual polyols and purified by reprecipitation with water from a DMF solution.

	Molecular Weight		
Polymer	$\textbf{Viscosimetry} \ (M_n)$	¹ H-NMR (M_n)	
PEG200-b-poly(AAm)	_	6200	
PEG400-b-poly(AAm)	7,200	6,500	
PEG4000- <i>b</i> -poly(AAm- <i>co</i> -VAc) DPETPEG200- <i>b</i> -poly(AAm- <i>co</i> -VAc)	240,000	$240,\!670$ $60,\!000$	

Table IIIMolecular Weight of Block Copolymers of PEG-b-poly(AAm)Determined by Capillary Viscosity and ¹H-NMR

As seen in Table IV, the polymerization yield of AN was about 80% when PEGs were used to reduce Ce(IV). The molecular weight of PEGbased block copolymers [PEG-*b*-poly(AN)]

$$\begin{array}{c} \mathsf{HOCH}_2\mathsf{CH}_2\mathsf{O}(\mathsf{CH}_2\mathsf{CH}_2\mathsf{O}) \underset{n}{\mathsf{CH}_2\mathsf{CH}} \overset{-}{\to} \mathsf{CH}_2\mathsf{CH} \overset{-}{\to} \mathsf{CH}_2\mathsf{CH} \overset{-}{\to} \mathsf{CN} \end{array}$$

PEG-b-Poly(AN)

increased with increasing molecular weight of PEG. However, the addition of a small amount of the VAc comonomer resulted in the molecular weight of PEG-based block copolymers not to be affected by the molecular weight of PEG.

The molecular weight of the copolymer was decreased from 160,000 to 33,000 while the polymerization yield was about the same when a halogenated (chloronated) polyol (XPEG) was used as the reducing agent in place of PEG400. This was probably due to the extensive chain transfer with XPEG. In this case, extensive chain branching would also be present in the copolymer. The molecular weight of the copolymer [PEG-*b*poly(AN)]



XPEG-b-Poly(AN)

could further be reduced to 14,000 by decreasing the AN monomer concentration while keeping the

Reducing	Monomer Concentration		Yield	Molecular
Agent	AN : VAc (mol/L)	Polymer	(%)	Weight
PEG200	1.5:0.00	PEG200-b-poly(AN)	81	142,000
PEG200	1.5:0.05	PEG200-b-poly(AN-co-VAc)	48	116,000
PEG400	1.5:0.00	PEG400-b-poly(AN)	80	160,000
PEG400	1.5:0.05	PEG400-b-poly(AN-co-VAc)	75	108,000
PEG600	1.5:0.00	PEG600-b-poly(AN)	82	166,000
PEG600	1.5:0.05	PEG600-b-poly(AN-co-VAc)	75	108,000
PEG1500	1.5:0.00	PEG1500-b-poly(AN)	80	315,000
PEG1500	1.5:0.05	PEG1500-b-poly(AN-co-VAc)	77	120,000
PEG4000	1.5:0.00	PEG4000-b-poly(AN)	78	220,000
PEG4000	1.5:0.05	PEG4000-b-poly(AN-co-VAc)	76	127,000
DPETEG ^a	1.5:0.05	DPETEG- <i>b</i> -poly(AN- <i>co</i> -VAc)	77	50,000
DPETDEG	1.5:0.05	DPETDEG- <i>b</i> -poly(AN- <i>co</i> -VAc)	77	87,000
DPETPEG200	1.5:0.05	DPETPEG200- <i>b</i> -poly(AN- <i>co</i> -VAc)	83	80,000
$\rm XPEG^{b}$	1.5:0.00	XPEG- <i>b</i> -poly(AN)	73	33,000
$\rm XPEG^{b}$	0.7:0.00	XPEG- <i>b</i> -poly(AN)	64	14,000

 Table IV
 Polymerization of AN with the Redox Pair of Polyol/Ce(IV)

Polymerization time = 2 h; temperature = 20°C; [polyol] = 20 g/L; [Ce(IV)] = 12 mmol/L.

^a Polymerization solvent = acetone : water (3:7).

^b XPEG concentration = 100 g/L.



Figure 4 FTIR absorbtion spectra of the water-insoluble copolymers on KBr pellets.

polymerization yield at about the same level (Table IV).

The FTIR spectra of the water-insoluble copolymer is shown in the Figure 4. The polyol OH stretching, C=N stretching, and polyol C-O-C stretching appeared at 3450, 2250, and 1120-950 cm^{-1} , respectively. The FTIR spectra of the copolymers of AN with 4% VAc, PEG600-b-poly(ANco-VAc), showed an additional carbonyl stretching band at 1740 cm^{-1} . The FTIR spectra of DPETEG-b-poly(AN-co-VAc) showed peaks at 1730 cm^{-1} due to C=O stretching with a small shoulder at 1740 cm^{-1} representing the acetate C=O stretching and at 730 cm⁻¹ due to C-H deformation of the aromatic ring. Halogenated poly(ether polyol)-poly(AN) copolymers, XPEG-bpoly(AN), showed characteristic strong multiple peaks at 670-840 cm⁻¹ due to carbon-halogen stretching.

The ¹H-NMR spectrum of the copolymers that were produced from the AN monomer showed the characteristic peaks at 2.08 δ ppm due to methylene protons and at 3.15 δ ppm due to methine protons of AN (Fig. 5). Methylene protons of the PEG moiety of the copolymers appeared as a small peak at 3.52 δ ppm. In the ¹H-NMR spectra of the copolymer PEG400-*b*-poly(AN-*co*-VAc), the acetate methyl groups resonated as a slightly singlet overlapping with the methylene groups which appear as a shift range at 2.08 δ ppm and methine protons of the VAc group was observed at 5.1 δ ppm. The ¹H-NMR spectra of the copolymer DPETEG-b-poly(AN-co-VAc) showed an additional integration intensity for the aromatic protons at 8.08 δ ppm and the two methylene protons of the carbon atom which are bonded to the oxygen of the ester groups appeared as a broad band at 4.3 δ ppm and the methine proton of acetate groups appeared at 4.7 δ ppm, respectively (Fig. 5). Similar peaks in the ¹H-NMR spectra of the copolymers of DPETDEG-b-poly(AN-co-VAc) were observed and the peaks due to methylene and me-



Figure 5 ¹H-NMR absorbtion spectra of the waterinsoluble copolymers in DMSO- d_6 .

	Molecula		
Polymer	M_w (Viscosity)	M_n (¹ H-NMR)	M_w/M_n (Calculation)
PEG200-b-poly(AN)	142,000	8,400	16.9
PEG200- <i>b</i> -poly(AN- <i>co</i> -VAc)	116,000	14,000	8.3
PEG600-b-poly(AN)	166,000	22,000	7.6
PEG1500-b-poly(AN)	315,000	70,000	4.5
PEG4000-b-poly(AN)	220,000	98,000	2.5

Table V Molecular Weights of PEG-b-poly(AN) Copolymers

thine protons appeared at 4.5 and 5.1 δ ppm, respectively.

The molecular weight of PEG-*b*-poly(AN) and PEG-*b*-poly(AN-*co*-VAc) copolymers were calculated from both ¹H-NMR signal ratios and the intrinsic viscosity of a dilute solution of corresponding copolymers. The signal at 2.08 δ ppm due to acrylonitrile methylene and at 3.52 δ ppm due to PEG methylene protons were used for the molecular weight calculations of copolymers. M_w/M_n values were in the range of radical polymerization²⁰ and decreased as the molecular weight of PEG unit increased (Table V).

Physical Properties of Polymers

Water Absorption

Water absorption and weathering properties of the block copolymers of PEG-*b*-poly(AN) are shown in Table VI. As expected, the water absorption of the copolymers increased as the molecular weight of the PEG block increased and reached to a value of about four times higher than that of the commercial copolymer. However, independent of the size of PEG, PEG-*b*-poly(AN-*co*-VAc) copolymers showed water-absorption values that are four times greater than those of the commercial copolymers.

The commercial poly(AN-*co*-VAc) copolymer is used for textile fiber production such as orlon. PEG-*b*-poly(AN-*co*-VAc) copolymers synthesized in this work may be used for the production of textile fiber with a much better water-absorption property than that of commercial poly(AN-*co*-VAc) fiber.

Weather Resistance

An accelerated weather test was carried out on the films of the block copolymers to determine their outdoor properties. After a 150-h test time, none of them was affected and no color changes were observed, indicating that the copolymers may be used for outdoor applications (Table VI).

Self-Extinguishing Character

Chlorinated poly(ether polyol)–poly(AN) block copolymers had self-extinguishing properties due to the presence of chlorine. These block copolymers may be used for textile fiber production in place of poly(AN-*co*-VAc) where self-extinguishing properties are desired.

Table VI Water Absorption and Weatherability Properties of Polymers

Polymer	Water Absorption (mg/cm^2)	Accelerated Weather Test Results (150 h)
PEG400- <i>b</i> -poly(AN)	1.6	No effect
PEG1500-b-poly(AN)	3.1	No effect
PEG4000-b-poly(AN)	3.9	No effect
PEG400-b-poly(AN-co-VAc)	3.9	No effect
PEG1500-b-poly(AN-co-VAc)	4.2	No effect
PEG4000- <i>b</i> -poly(AN- <i>co</i> -VAc)	3.8	No effect
DPETPEG200- <i>b</i> -poly(AN- <i>co</i> -VAc)	0.6	No effect
Poly(AN-co-VAc) ^a	0.9	No effect

^a Commercial poly(AN-co-VAc) has a molecular weight of 120,000.



Figure 6 Effect of shear rate on apparent viscosity of 2% polyol-*b*-poly(AN) solutions in DMF at 27°C: (\bigcirc) XPEG-*b*-poly(AN); (x) PEG1500-*b*-poly(AN); (\blacksquare) PEG400-*b*-poly(AN); (\triangle) DPETPEG200-*b*-poly(AN-*co*-VAc); (\bigcirc) PEG400-*b*-poly(AN-*co*-VAc); (\Box) PEG1500-*b*-poly(AN-*co*-VAc); (\Box) ommercial poly(AN-*co*-VAc).

Rheological Characteristics

Rheological properties of the copolymers were compared with the corresponding vinyl polymers by measuring their solution viscosities in a Brookfield rotational viscometer, type RV II. The results are shown in Figure 6. The viscosities of water-insoluble block copolymers were determined as a 2% dimethylformamide solution at 27°C. Their solutions behaved like non-Newtonian liquids. The rheological properties of the solution are affected by the molecular weight and the concentration of the solutions. PEG-b-poly-(AN) copolymers were dilatant, the same as the Poly(AN) homopolymer. Increasing viscosity with the increasing shear rate characterizes dilatant fluids. Dilatancy is also referred to as shear-thickening flow behavior. Polyol-b-poly(AN-co-VAc) and XPEG-b-poly(AN-co-VAc) showed pseudoplastic (shear-thinning) properties similar to those of poly(AN-co-VAc). The viscosity of the pseudoplastic solutions decreased with an increasing shear rate. Unexpectedly, the viscosity of XPEG-b-poly(AN-co-VAc) with a molecular weight of 33,000 was about 10 times higher than poly(AN-co-VAc) with a molecular weight of 120,000.

CONCLUSIONS

The redox pairs consisting of different polyol reductants and Ce(IV) were used to produce block copolymers of polyols and vinyl monomers. Water-soluble block copolymers of PEG-*b*-poly(AAmco-VAc) and polyol depolymerized PET-b-poly-(AAm-co-VAc) were easily produced with this method. PEG-b-PAAm copolymers may be used in the area of poly(AAm) applications where the ability of the associative complex formation of the PEG moiety is an advantage. The application area may include the printing ink, textile, adhesive, emulsifier, and dispersant industries. Besides, these water-soluble copolymers contain hydroxyl groups coming from reducing polyols so they may find applications in the area of the production of polyurethanes with higher water absorption. Water-insoluble block copolymers such as PEG-b-poly(AN-co-VAc) and halogenated polyol-bpoly(AN-co-VAc) obtained in this work could be used to produce textile fiber with better water-absorption and self-extinguishing properties.

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