ANIONIC POLYMERIZATION OF MONOMERS BEARING QUATERNARY AMMONIUM GROUPS
1. POLYMERIZATION OF METHACRYLATE DERIVATIVES

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SUMMARY: Amphiphilic surface-active vinyl monomers alkyl[2-(methacryloyloxy)ethyl]dimethylammonium bromides, where alkyl is butyl or dodecyl have been investigated with respect to their polymerization behavior in the presence of various anionic initiators (Bu_2Mg, *tert*-BuOK, calcium amide alkoxide). In most cases, the products consist of a low-molecular-weight fraction (M_w up to 5000) and a high-molecular-weight fraction (M_w up to 120 000). Block copolymers of the quaternary ammonium monomers with ethylene oxide show associative behavior in aqueous solutions.

INTRODUCTION

Production of cationic water-soluble homopolymers and copolymers has grown rapidly during the recent years because of their commercial applications (Ref. 1). Amphiphilic surfactant monomers are widely used as reactive monomers in radical polymerization for synthesis of novel materials and for polymerization in structurally ordered media (Refs 2-7).

Polymerization of alkyl[2-(methacryloyloxy)ethyl]dimethylammonium bromides (with alkyl C_{12}, MEDA-C_{12} or with alkyl C_4, MEDA-C_4) initiated with radical initiators both in polar and nonpolar media as well as their spontaneous polymerization have been described (Refs 8-10). Anionic polymerization (AP) of methacrylate-containing quaternary ammonium salts (QAS-M) would provide a possibility of obtaining block copolymers carrying cationic blocks and thus of diversifying both the materials formed and their properties. Moreover, the preparation of block copolymers of QAS-M and ethylene oxide through AP is a simple procedure compared with the radical polymerization which may require high-cost operations (Ref. 11). Our previous investigations of AP of methyl methacrylate in the presence of QAS have clearly shown that these additives, though not hindering the process, greatly affect the structure of the polymers formed (Refs 12-15). Therefore it can be assumed that incorporation of a quaternary ammonium group into the monomer molecule will not terminate the propagation in AP.

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This paper describes our results on the AP of alkyl salts of MEDA with different alkyl lengths as well as their copolymers with ethylene oxide. Some details on solubility and associative properties of the products obtained are discussed in terms of their molecular structure.

Experimental

Materials

Purification of solvents (toluene and THF) is described elsewhere (Ref. 16).

Monomers MEDA-C_{12} and MEDA-C_4 were prepared according to Ref. 17. Their benzene solutions were freeze-dried in the reaction vessel, directly before polymerization.

From a 1.0 M solution of Bu_2Mg in heptane (Aldrich) under argon, heptane was evaporated using the high-vacuum line technique, the initiator was dissolved in toluene and distributed into ampoules provided with break-seals. The concentration of Bu_2Mg was determined by hydrolysis in excess of 0.1 M HCl and by titration with 0.1 M NaOH using phenolphthalein as indicator.

Alkoxide-modified calcium amide initiator (AlkCaA) was synthesized directly in the reaction vessel by the reaction of Ca and ethylene oxide in liquid NH_3 (Ref. 18).

The preparation of *tert*-BuOK was performed according to the procedure described in Ref. 19. Methanol, diethyl ether and acetone were dried over BaO.

Methods

^1H and ^{13}C NMR spectroscopy were performed on a Bruker WM 250 spectrometer at room temperature and at 50-80 °C.

HPLC was performed on a Waters liquid chromatograph equipped with an M 510 pump, a U6K universal injector, a μ Bondapak C_{18} (300 x 3.9 mm) analytical column and a photodiode array detector M 991. MeOH/H_2O (3/2 v/v) was used as eluent at room temperature and at a flow rate of 0.4 mL/min. 0.05 mL of polymer solution (0.004-0.006 g/mL) was injected into the system.

Size exclusion chromatography (SEC) with double detection was performed at 40 °C on a chromatography line consisting of an M 510 pump, a U6K universal injector, two Ultrahydrogel columns with pore sizes of 120 Å and 250 Å, a differential refractive index detector M 410, and a tunable absorbance detector M 486 (all Millipore Co., Waters Chromatography Division). MeOH/H_2O 1/4 (v/v) was used as eluent at 40 °C and at a flow rate of 0.8 mL/min. Molecular weight characteristics of the polymers were calculated using a "universal calibration" curve constructed with monodisperse poly(oxyethylene) (POE) and poly(ethylene glycol) (PEG) standards.

Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) *mass spectrometry* was carried out on a MALDI-TOF Voyager-DE Biospectrometry work station (PerSeptive Biosystems, Framington, MA) spectrometer, incorporating a 337-nm nitrogen laser. The instrument was operated in linear mode with an accelerating potential of positive 25 kV. The matrix was indole-3-acrylic acid at a concentration of 0.2 M in DMSO (Fisher Scientific). The samples were dissolved in DMSO at 1.10^{-4} M. To obtain the best MALDI mass spectrum, various experiments with different polymer/matrix molar ratios (1:10, 1:5, 1:2) were performed. Bovine serum insulin was used for calibration. Molecular weights were calculated using the "Polymer page" of Galaxy software. All spectra were smoothed with a 5-19-point Golay - Savitsky smoothing algorithm.

Viscosity measurements were performed in an Ubbelohde capillary viscometer. Specific viscosities of copolymers were measured in aqueous solutions at 30 °C at polymer concentrations 0.08-0.032 g/dL, the basic solution being directly diluted in the viscometer. Molecular weights were calculated from the equation $[\eta]=1.25x10^{-4}M^{0.78}$ (Ref. 20).

Apparent viscosity experiments were performed on a Brookfield model LVT viscometer equipped with two different sizes of spindles (Nos 2 and 3) and a temperature-controlled water bath at 25 °C. The viscosities in centipoise were determined at rotational speed of the spindle in the range of 0.3-60 rpm in 1% aqueous solutions of polymers.

Light scattering (LS) measurements were performed in the GPC mode in a system equipped with a solvent delivery system M 590 Waters, a U6K Waters manual injector, two GPC columns - Type E and Type F (IBM Instrument Inc.), an interferometric refractometer Optilab DSP (Wyatt Technology Co.) and a multi-angle laser light-scattering detector (MALLS) DAWN DSP laser photometer (Wyatt Technology Co.). The measurements were made at a wavelength of 488 nm at 50 °C and 1 mL/min flow rate at sample concentrations (0.001 – 0.003) x 10^{-3} g/mL.

Polymerization

The polymerizations with Bu_2Mg and *tert*-BuOK as initiators were carried out using the high-vacuum line technique (10^{-3} Pa) in the reaction vessel described previously (Ref. 16). The monomer was dissolved in toluene or THF at appropriate temperature and then an initiator solution was added. After a given time, the polymerization was terminated by adding methanol containing an HCl equivalent to the Mg^{2+} or K^+ amount. The polymer was precipitated in acetone on cooling, collected by filtration, washed with acetone, and dried in vacuum.

Homopolymerization of MEDA-C_{12} and copolymerization with ethylene oxide initiated with AlkCaA were carried out in a four-necked flask, fitted with a mechanical stirrer, condenser, thermometer and inlet tube, purged with dry argon at ambient pressure. Liquid ammonia (35 ml) was added into the reaction vessel, 0.25 g of Ca was dissolved and converted into AlkCaA after adding ethylene oxide. After evaporation of ammonia, heptane (15 ml) was added, the residue was dispersed in 55 ml solution of MEDA-C_{12} (0.1 M) in THF and the reaction mixture was stirred at 20 °C for 4 h. A sample of the homopolymer was taken. Then ethylene oxide was slowly bubbled at 17 °C under stirring for 4 h to prepare a block copolymer of MEDA - ethylene oxide. The solution was filtered, the precipitated copolymer in acetone was separated by filtration, then washed with cold acetone and dried.

The other procedure provided an alternative method of copolymerization with POE as a first block. AlkCaA was prepared, then heptane or THF (20 ml) was added and the suspension was cooled to 17 °C. Feeding with ethylene oxide for an appropriate time (10 min - 4 h) was performed, an 0.1 M solution of MEDA-C_{12} in THF (65 mL) was added and the reaction mixture was stirred at 17 °C for 1 - 4 h. The product was isolated, thoroughly washed with petroleum ether and diethyl ether, dried, extracted with cold absolute ethanol, again dried and analyzed.

RESULTS AND DISCUSSION

I. Anionic polymerization of MEDA-C_{12}

Polymerization conditions and product molecular weights as determined by SEC and MALDI-TOF are presented in Table 1.

Table 1. Anionic polymerization of MEDA-C_{12} and its copolymerization with ethylene oxide (17 °C, 4 h)

Initiator/solvent	Yield %	SEC[a]		MALDI-TOF[b]		LS[c]	
		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$
				homopolymers			
AlkCaA/heptane-THF	50	high MW 1000[d]	high MW 1200	34 200 1700	34 800 3300	- -	- -
Bu_2Mg/THF[e]	30	2700	5300	-	-	-	-
Bu_2Mg/toluene	20	33 000 2100[d]	70 000 2700	62 200 6300	63 600 7600	308 300 36 200	338 700 62 600
				copolymer			
AlkCaA/heptane-THF	-	86 000	120 000	80 500	99 300	743 900 23 200[a]	1 247 000 46 900

[a] $MeOH/H_2O$, [b] DMSO, [c] DMF, [d] low-MW fraction, [e] 24 h

1. *Initiation with alkoxide-modified $Ca(NH_2)_2$ in THF*

HPLC chromatogram of the polymer formed at 20 °C after 4 h is presented in Fig. 1.

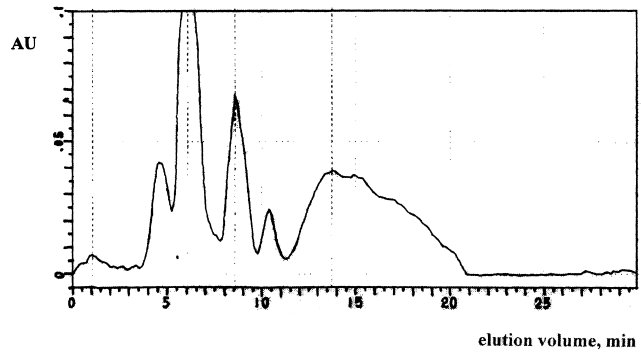


Fig. 1. HPLC chromatogram of poly(MEDA-C_{12}) prepared with alkoxide-modified $Ca(NH_2)_2$ as initiator (eluent CH_3OH/H_2O 3/2 v/v)

The chromatogram consists of three groups of peaks with identical UV spectra (λ_{max} 210-220 nm). The first and second group of peaks can be assigned to low-molecular-weight fractions while the third broad peak (12-20 min) can be attributed to fractions of higher molecular weights.

The product estimated by SEC consists of two fractions, a low-molecular-weight one and a fraction of high molecular weight (>150 000). The result was confirmed by MALDI-TOF mass spectrometry: the method proved the existence of two fractions, the high-molecular-weight (M_n 34 200) (Fig. 2) and the low-molecular-weight fraction which shows peaks between the molecular weight of the monomer unit and 3500.

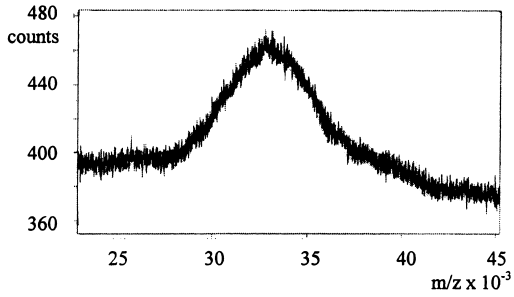


Fig. 2.
MALDI-TOF mass spectrum of high-MW poly(MEDA-C_{12}) prepared with alkoxide-modified $Ca(NH_2)_2$ as initiator

Figure 3 is a ^1H NMR spectrum of the product. There are no signals of CH_2=C protons (5.72 and 6.15 ppm) and CH_3-C=CH_2 (1.97 ppm) bonds whereas the other signals correspond to those of the monomer unit, which suggests that the polymerization has proceeded.

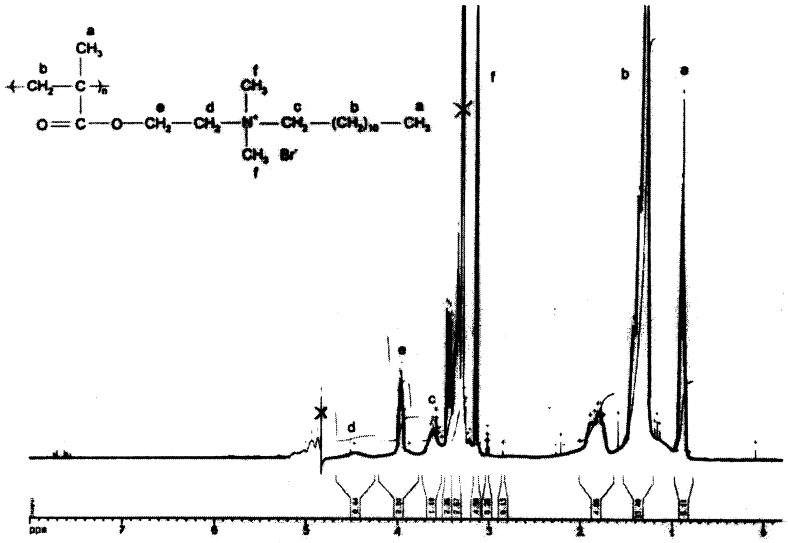


Fig. 3. ^{1}H NMR spectrum of poly(MEDA-C_{12}) in CD_3OD prepared with alkoxide-modified $Ca(NH_2)_2$ as initiator

2. *Initiation with Bu_2Mg*

a) polymerization in THF

An HPLC plot (Fig. 4) of the product shows a signal at retention time of 11 min, which can be assigned to oligomers. Indeed, the SEC traces obtained in $MeOH/H_2O$ reveal the formation of a low-molecular-weight product (MW 2700-5300) with UV spectrum typical of the monomer. The results obtained by ^{1}H and ^{13}C NMR are analogous to those for the polymers formed with an alkoxide-modified $Ca(NH_2)_2$ as initiator.

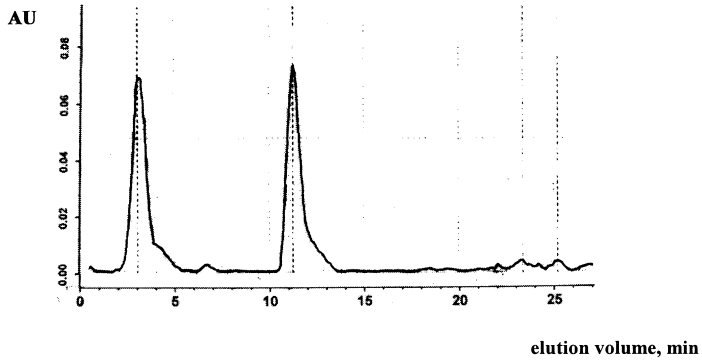


Fig. 4. HPLC chromatogram of poly(MEDA-C_{12}) prepared with Bu_2Mg initiator in THF . (eluent CH_3OH/H_2O, 3/2 v/v) .

b) polymerization in toluene

The HPLC eluogram has a profile characteristic of polymers prepared with other initiators.

SEC investigation of the soluble part of the polymer points to the formation of a high-molecular-weight fraction ($\overline{M}_n$ = 33 000, $\overline{M}_w$ = 70 000) and a low-molecular-weight fraction ($\overline{M}_n$ = 2100, $\overline{M}_w$ = 2700) (Table 1).

The MALDI-TOF mass spectrum shows a high-molecular-weight polymer fraction in accordance with the result obtained by SEC.

The higher values of molecular weights obtained with LS in DMF are most likely a result of formation of aggregates due to strong interactions of ionic groups in this solvent.

The ^{1}H and ^{13}C NMR results prove that the anionic polymerization proceeds through a nucleophilic attack on the $CH_2=\overset{|}{C}-$ bond.

3. *Initiation with tert-BuOK in toluene*

The product obtained has not been accurately characterized due to its extremely poor solubility in common solvents.

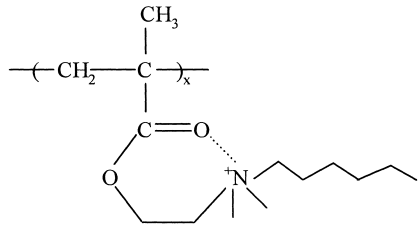
II. **Polymerization of MEDA-C_4**

initiated with Bu_2Mg in THF

The HPLC chromatogram of the product obtained shows the existence of a signal at retention time 11 min followed by a broad signal, most probably due to the formation of oligomers and polymers of different molecular weights (UV spectra are identical). Unfortunately, SEC could not be performed due to the insolubility of the product in the eluent used.

Though the products formed both in THF and toluene remain generally in solution, their solubility in THF, toluene, chloroform, methanol and methanol-water, after isolation and drying, becomes almost negligible. Such a behavior has been reported before (Refs 21-24). It seems that ionic groups are tightly bound within a hydrophobic network in the solid state and may form microphase-separated domains. Indeed, the carbonyl group is closely linked to the ionic head group being probably intramolecularly associated with the ammonium cation, in agreement with the conformationally rigid and compact model proposed for the head group of poly(QAS-M) presented in Scheme 1 (Ref. 17).

With increasing molecular weight, the solubility of the polymers decreased due to the formation of more stable compact intra- and/or intermolecular aggregates.



Scheme 1. Six-membered ring structure formed via intramolecular interaction between the ester carbonyl group and the onium nitrogen atom.

III. Block copolymerization of MEDA-C_{12} and ethylene oxide initiated with alkoxide-modified $Ca(NH_2)_2$ in THF

To enhance the solubility of the polymers and to obtain water-soluble associating polymers, further studies were performed of copolymerization of MEDA-C_{12} with ethylene oxide using a Ca-based catalyst system.

Alkoxide-modified calcium amides are the most effective catalysts for preparation of superhigh-molecular-weight POE (Ref. 18). Moreover, the catalysts are very active at temperatures below the melting point of POE. Thus the synthesis of POE resins can be most effectively realized by precipitation polymerization. The reaction medium (hydrocarbons or THF) at temperatures below 20 °C dissolves only the monomer.

MEDA-C_{12} is soluble in THF. This solvent precipitates high-molecular-weight POE at temperatures below 20 °C, which makes it an appropriate organic medium for precipitation polymerization and for copolymerization of ethylene oxide.

1. *Preparation of poly(MEDA-C_{12})-block-POE copolymer*

The first route was to prolong the experiment described in section I.1 by bubbling ethylene oxide through the reaction mixture at 20 °C for additional 4 h. The product formed has a much better solubility in MeOH/H_2O (1/4 v/v) and dissolves almost completely in pure water.

Its HPLC spectrum resembles that of homopoly(MEDA-C_{12}) (POE block is not visible) but there is a difference in the spectrum mode: it is "dragging" throughout the whole elution volume unlike the spectrum of homopoly(MEDA-C_{12}) which contains an evident fraction in the range of 15-20 min.

SEC traces show the formation of a high-molecular-weight polymer ($\overline{M}_n$ = 86 000, $\overline{M}_w$ = 120 000). The elution volume of the first block, poly(MEDA-C_{12}), is higher than that of the copolymer formed by copolymerization with ethylene oxide. Obviously, these SEC conditions

are not suitable for determination of the molecular weight characteristics of high-molecular-weight homopoly(MEDA-C_{12}), most likely as a result of the formation of micelles and/or aggregates in MeOH/H_2O. The latter process modifies the hydrodynamic volume of the polymer molecule. As it was mentioned above in section I.2b, this is the reason for the extremely high molecular weight of copolymer as obtained by LS measurements in DMF where this effect is obviously much more pronounced (see Table 1).

A comparison of the data from the MALDI-TOF analyses (Table 1) of homopoly(MEDA-C_{12}) with those of the final copolymer indicates a considerable increase in molecular weight of the copolymer (homopolymer $\overline{M}_n$ = 34 000, $\overline{M}_w$ = 35 000; copolymer $\overline{M}_n$ = 78 500, $\overline{M}_w$ = 97 500).

The ^{1}H NMR spectra also support the formation of poly(MEDA-C_{12})-*co*-POE copolymer by the appearance of signals at 3.6 ppm which are due to OCH_2 units in the polymer chain (Fig. 5).

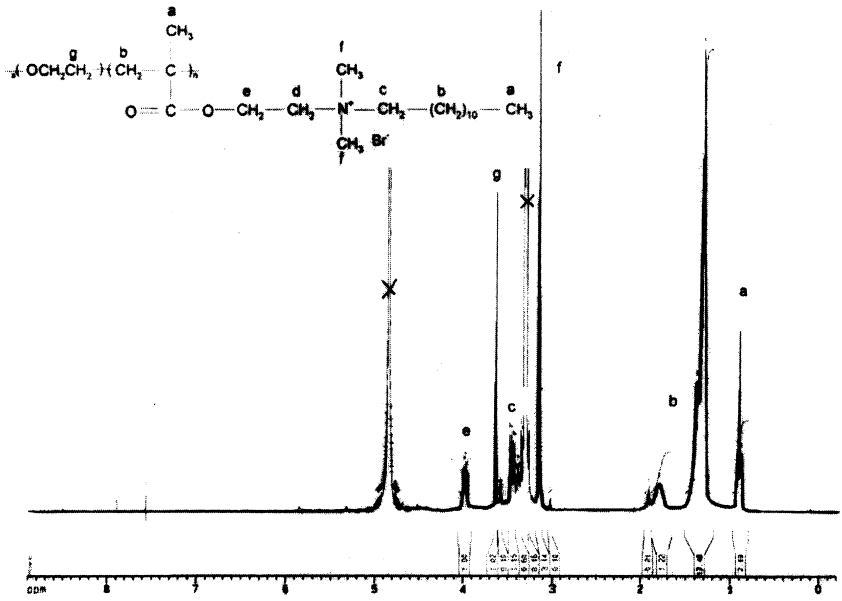


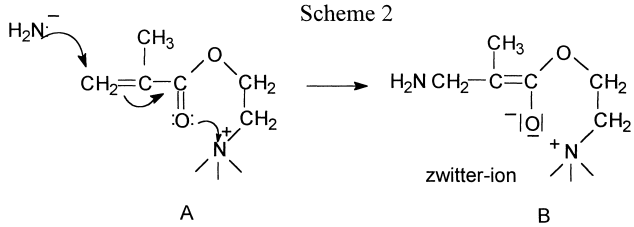
Fig. 5. ^{1}H NMR spectrum of poly(MEDA-C_{12})-*co*-POE in CD_3OD prepared with with alkoxide-modified $Ca(NH_2)_2$ as initiator

2. *Preparation of poly(MEDA-C_{12})-co-POE block and random copolymers*

The second route was aimed at carrying out a heterogeneous coordination copolymerization with POE as the first block. This approach is unusual as it is well known that the growing species, alkoxide anions, obtained by AP of ethylene oxide, are not very efficient in addition

reactions to double bonds of vinyl monomers. As a matter of fact, the introduction of a quaternary ammonium group significantly affects the methacrylate monomer reactivity. The electron density on the vinyl bond is considerably reduced by the electron-withdrawing effect of the quaternary group; thus the extension of the π-conjugated system from the vinyl group may speed up the polymerization. The increased monomer reactivity correlates with the reduced effectivity of the anionic living ends derived from the vinyl-QAS monomer (Scheme 2) (Ref. 9).

Scheme 2



The onium center in A activates the double bond in the reaction while after the attack of the NH_2^- anion, the resulting adduct is deactivated forming a zwitter-ion B. The reduced activity of the anionic living polymers of a methacryloyl-QAS monomer is demonstrated by the results of sequential copolymerization with ethylene oxide as summarized in Table 2.

Table 2. Sequential copolymerization of ethylene oxide (EO) and MEDA-C_{12} with alkoxide-modified $Ca(NH_2)_2$ catalyst

MEDA-C_{12} g	Time h	Yield [a] g	MEDA-C_{12} [b] mol %	[η] [c] dl/g	η [d] cP	Note
- [e]	4	28.2 (-)	-	10.73	800	-
2 [f]	6	13.8 (12.2)	0.4	14.40	1400	EO feeding and QAS-M at the start
3 [f]	4+4	12.7 (11.4)	0.3	-	300	EO feeding 4 h, QAS-M 4 h
1 [g]	1+1	9.0 (8.6)	0.9	11.05	600	EO feeding 1 h, QAS-M 1 h (25 °C)

[a] The yield after EtOH extraction is in parentheses, [b] by NMR, [c] H_2O, 30 °C, [d] 1% aqueous solutions (Brookfield, 25 °C), [e] 1.00 g Ca, 17 °C, heptane-THF 1/3 (v/v); M_v=2.1x10^6, [f] 0.25 g Ca, 15 °C, heptane-THF 1/3 (v/v), [g] 0.25 g Ca, 15 °C, THF

An indirect indication of the inclusion of MEDA-C_{12} in the copolymers was obtained by following in the UV spectra the anion exchange in THF solutions of lithium picrate (LiPi) after adding the block copolymer (Table 3).

Table 3. Absorption maxima (λ_{max}) of lithium picrate (LiPi) and poly(oxyethylene)s in THF

Solute	λ_{max} (nm)
LiPi	350
LiPi + POE homopolymer	352
LiPi + POE-*co*-poly(MEDA-C_{12})	364

A shift of the LiPi absorption maximum larger than the shift in the presence of neat POE homopolymer occurs in the presence of the block copolymer.

The presence of the hydrophobic dodecyl group and QA group in MEDA-C_{12} units of the block copolymer affects the viscometric behavior of aqueous solutions of the copolymers obtained in the presence of typical surfactants, sodium dodecyl sulfate (SDS) and Brij 78 (Fig. 6 and Table 4).

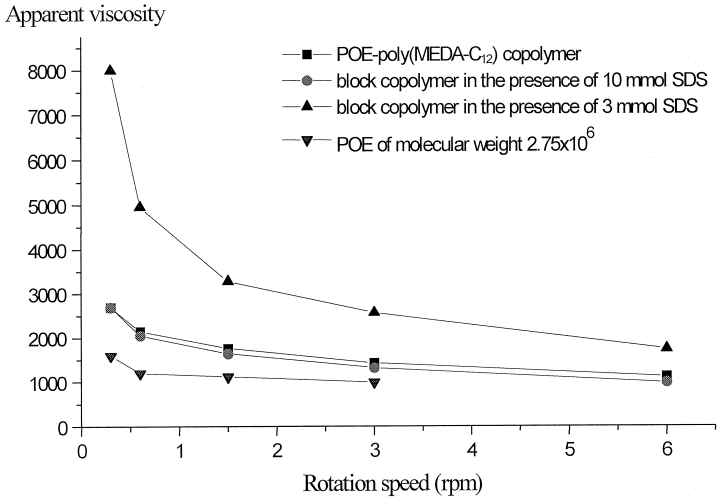


Fig. 6. Effect of rotation speed on viscosity of aqueous solutions of poly(oxyethylene)s (1%, 25 °C)

Table 4. Viscometric properties of aqueous solutions of MEDA-C_{12} - ethylene oxide copolymers

POE		POE-*co*-poly(MEDA-C_{12})		POE-*co*-poly(MEDA-C_{12}) + 3 mmol SDS		POE-*co*-poly(MEDA-C_{12}) + 3 mmol Brij 78
[η] dl/g	η P	[QAS] mol %	[η] dl/g	η (cP)		η (cP)
12.9	35	0.5	14.1	3500	6600	5400
10.2	29	0.9	14.3	3000	4000	4200

As can be seen by comparing the results for neat POE with those for POE-*co*-poly(MEDA-C_{12}) (Table 4), after QAS-M incorporation, the value of the intrinsic viscosity increases whereas the Brookfield viscosity of 1 wt % aqueous solutions does not change significantly. In the presence of a surfactant at a concentration of 3 mmol/L, η increases, the effect being more pronounced in the case of anionic SDS. Aqueous solutions of the block copolymer show pseudoplastic behavior. The apparent viscosities decrease with increasing rotation speed as shown in Fig. 6. But even at high rotation speeds, the viscosity remains higher than that of a homopolymer of comparable molecular weight due to hydrophobic interactions which contribute to viscosity. The viscosity is restored after removing the shear, which is typical of associating polymers.

CONCLUSION

Homopolymers of MEDA-C_n (n = 4, 12) were obtained by anionic polymerization using various anionic initiators in polar and nonpolar media. In most cases, the polymer contains two fractions; after drying, the high-molecular-weight fraction shows a lower solubility in common solvents most probably due to intramolecular association in the solid state.

It was proved that methacrylate-containing quaternary ammonium salts may copolymerize with ethylene oxide in THF at 15-17 °C to form block as well as random poly(QAS-M)-POE copolymers, which are more soluble in common solvents than poly(QAS). A viscosity enhancement of their aqueous solutions was established. Higher yields and molecular weights are achieved using sequential polymerization (in which POE appears as a first block) with alkoxide-modified $Ca(NH_2)_2$ as a catalyst.

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