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Polymer 42 (2001) 2745–2753

polymer

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Nonionic hydrogels by copolymerization of vinylene carbonate and oligo(ethylene glycol) vinyl ethers

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Received 17 August 2000; received in revised form 19 September 2000; accepted 19 September 2000

Abstract

Bulk polymerization of vinylene carbonate (VCA) with ethylene glycol monovinyl ether (EMVE), diethylene glycol monovinyl ether (DMVE) and methyl triethylene glycol vinyl ether (MTVE), respectively, was carried out. Compared with DMVE and MTVE, the yield of the VCA copolymer with EMVE was low due to a side reaction of acetalization. The copolymerization of MTVE with VCA has been shown to produce linear copolymers and alternating copolymers have been found to form at a 1:1 molar monomer ratio. The copolymerization of EMVE and DMVE with VCA, on the other hand, generally yielded crosslinked copolymers. The reason may be a radical transfer reaction that occurred at methylene groups adjacent to hydroxyl groups of pendent oxyethylene moieties, as inferred from studying the swelling behavior of hydrolyzed copolymers in acidic aqueous solution. The copolymers and their hydrolysis products, especially copoly(MTVE/VCA) and copoly(DMVE/VCA), exhibited low glass transition temperatures, which is apparently due to flexible pendent groups on polymer chains. The copolymerization in the presence of oligo(ethylene glycol) divinyl ethers as crosslinking agents followed by hydrolysis with a 5 wt.% NaOH solution gave rise to the formation of three different nonionic hydrogels. The swelling behavior of all the gels was found to be independent of the presence of some electrolyte salts at various concentrations in an aqueous solution. However, the hydrogels based on copoly(EMVE/VCA) and copoly(DMVE/VCA) were shown to be unstable under acidic conditions, whereas those based on copoly(MTVE/VCA) were found to be only slightly influenced by the pH value of an aqueous medium.

Keywords: Vinylene carbonate; Oligo(ethylene glycol) vinyl ethers; Radical copolymerization

1. Introduction

In recent years, hydrophilic gels, briefly called hydrogels, have found numerous applications in various fields, such as sanitary materials, ingredients for paints or adhesives, cosmetics, food industry, water-retaining agents in agriculture, sealing or packing materials, separation membranes, contact lenses and drug delivery systems [1–6]. Most hydrogels are ionic networks that have anionic (e.g. carboxylic and sulfonic acids) or cationic (e.g. amines and their salts) groups chemically bound to their skeleton. However, the swelling capacity of ionic hydrogels is known to be sensitive to the presence of electrolytes and a small amount of some salts in external solution may cause a swollen hydrogel to collapse [7]. Therefore, several kinds of nonionic networks were prepared in a search for electrolyte-stable hydrogels on the basis of poly(*N*-vinyl pyrrolidone) [8], poly(acrylamide) [9], poly(ethylene glycol) [10], and poly(2-hydroxyethyl methacrylate) [11].

Generally, the polymerization of vinyl ethers via a radical mechanism cannot produce polymers with a high molecular weight [12]. The reason for the poor radical polymerizability of vinyl ethers is considered to be an instability of propagating radical species due to the lack of resonance stabilization by the neighboring alkoxy group, which results in frequent hydrogen abstraction [13]. Vinyl ethers are typical electron-donating monomers and thus polymerize selectively via a cationic polymerization mechanism, which has been extensively studied in recent years [14,15]. On the other hand, it is well known that certain free radical copolymerization systems comprising both electron-donating and electron-accepting monomers can produce alternating copolymers [16–18]. Due to a strongly electrophilic character of a double bond in vinylene carbonate, this monomer was reported to readily copolymerize with vinyl ethers to bring about the formation of alternating copolymers [19,20]. Unlike most disubstituted ethylenes, vinylene carbonate can homopolymerize through a radical

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0032-3861/01/$ - see front matter
PII: S0032-3861(00)00685-6

Table 1
Bulk copolymerization of vinylene carbonate and oligo(ethylene glycol) vinyl ethers (OGVE) at 60°C

Sample no.		OGVE (g)	VCA (g)	AIBN (g)	Total yield (g)	Crosslinked fraction (g)	Soluble fraction (g)
E-5	EMVE	2.60	2.40	0.0060	0.50	0	0.50
E-6		2.60	2.40	0.0100	0.82	0	0.82
E-7		2.60	2.40	0.0200	1.50	0	1.50
E-8		2.60	2.40	0.0300	2.10	0.70	1.40
E-9		2.60	2.40	0.0513	3.00	2.00	1.00
D-7	DMVE	3.10	1.90	0.0060	0.58	0.58	0
D-8		3.10	1.90	0.0100	4.10	4.10	0
D-9		3.10	1.90	0.0200	4.21	4.21	0
D-10		3.10	1.90	0.0300	4.40	4.40	0
D-11		3.10	1.90	0.0438	4.60	4.60	0
M-5	MTVE	3.50	1.50	0.0060	1.34	0	1.34
M-6		3.50	1.50	0.0150	2.21	0	2.21
M-7		3.50	1.50	0.0380	3.16	0	3.16
M-8		3.50	1.50	0.0400	3.57	0	3.57
M-9		3.50	1.50	0.0500	4.25	0	4.25
M-10		3.50	1.50	0.0537	4.34	0	4.34

mechanism [21,22]. The reactive cyclic carbonate groups of poly(vinylene carbonate) chains offer some opportunities for application, for instance, as active supports for biomolecules [23,24] and ionically conducting polymer electrolytes for lithium batteries [25,26]. Furthermore, cyclic carbonate groups can easily be hydrolyzed under basic conditions to afford vicinal hydroxy-groups, which can enhance hydrophilicity of the resulting polymers. Accordingly, a nonionic hydrophilic polymer may be produced.

The present paper reports on the synthesis of new hydrogels via copolymerization of vinylene carbonate with three hydrophilic oligo(ethylene glycol) vinyl ethers, viz. ethylene glycol monovinyl ether (EMVE), diethylene glycol monovinyl ether (DMVE), and methyl triethylene glycol vinyl ether (MTVE) followed by hydrolysis of the copolymers. Their swelling behavior has also been studied.

2. Experimental

2.1. Materials

Ethylene glycol monovinyl ether (EMVE), diethylene glycol monovinyl ether (DMVE), methyl triethylene glycol vinyl ether (MTVE), diethylene glycol divinyl ether (DDVE), tetraethylene glycol divinyl ether (TDVE) all from BASF AG were distilled in vacuum before use. Vinylene carbonate (VCA) purchased from Aldrich was purified by distillation under reduced pressure. 2,2′-Azoisobutyronitrile (AIBN) was recrystallized from methanol.

FTIR and ^{1}H NMR spectra were recorded on Bruker IFS 88 and Bruker DPX 360 spectrometers, respectively. DSC measurements were performed on a Thermal Analyzer 2000/DSC 912 heat-flow instrument at a heating rate of 20°C/min.

2.2. Polymerization of VCA and vinyl ethers

Copolymers of VCA and vinyl ethers were obtained by bulk polymerization at 60°C for 18 h in the presence of different amounts of initiator, i.e. AIBN. Different amounts of both monomers and AIBN were mixed in glass tubes and after the initiator was fully dissolved in the mixture of monomers, the glass tubes were flushed with nitrogen, sealed and heated at 60°C in an oil bath for 18 h. The resulting products were precipitated in (or extracted with) methyl *tert*-butyl ether and dried in vacuum at 70°C. The composition of the copolymers was calculated from their ^{1}H NMR spectra.

2.3. Synthesis of hydrogels

The crosslinked copolymers of VCA and oligo(ethylene glycol) vinyl ethers were prepared according to the conditions presented in Table 3. The copolymers were cut into pieces of ca. 1 mm thickness and treated with a 5 wt.% aqueous NaOH solution at room temperature to hydrolyze for 12 h. Subsequently, the samples were repeatedly immersed in a large excess of distilled water to remove the residual NaOH until washings became neutral. Finally, the hydrogels were dried under reduced pressure at 70°C to constant weight.

2.4. Swelling measurements

A series of aqueous solutions of various electrolyte salts, viz. $CaCl_2$, LiCl, KCl, NH_4Cl, $N(CH_3)_3BzCl$ (trimethyl benzyl ammonium chloride), Na_2SO_4, and sodium acetate, as well as HCl and NaOH were prepared. Dry hydrogel samples were transferred to each of the aqueous solutions and were allowed to swell to equilibrium. The weight uptake of the hydrogels was then measured. The swelling degree

Table 2
Swelling degrees (g/g) of hydrolyzed copolymers of VCA with oligo(ethylene glycol) vinyl ethers in aqueous solution at various pH values. (All hydrogels were kept in an excess of aqueous solutions for one week)

Gels[a]	pH						
	1 M HCl	1.00	2.00	4.00	7.00	9.00	1 M NaOH
E-2	Soluble[b]	Soluble[b]	Soluble[b]	Soluble[b]	19.8	19.7	18.9
D-6	19.1	18.8	18.6	18.8	16.9	16.8	16.1
D-1	Soluble[b]	Soluble[b]	Soluble[b]	Soluble[b]	21.0	20.6	20.5
M-1	31.3	31.0	30.7	30.2	29.0	28.7	27.4

[a] See Table 3.
[b] The gel decomposes to yield soluble products.

was calculated from the following expression:

$$S_{wt} = W_e/W_0$$

where W_e and W_0 are the weight of swollen hydrogel at equilibrium and that of the original sample, respectively.

3. Results and discussion

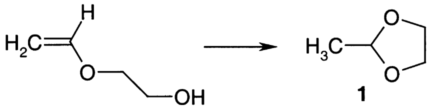
3.1. Copolymerization of vinyl ethers and VCA

The data concerning the copolymerization of vinylene carbonate and oligo(ethylene glycol) vinyl ethers (OGVE), viz. the amount of monomers and the yield of copolymers, are listed in Table 1. The results show that with increasing amount of AIBN, the yield of copolymers increased. Furthermore, the copolymerization of VCA with DMVE or MTVE afforded substantially higher yield as compared to that of VCA and EMVE. It was found that vinyl ethers are very sensitive to hydrolysis and a small amount of water in a copolymerizaton system may cause them to decompose, producing acetaldehyde and corresponding alcohol or glycol. Thus, during the copolymerization of VCA and vinyl ethers, the evolution of acetaldehyde could be detected because of traces of water still present in the monomers.

In the case of the copolymerization of VCA and EMVE, yet another side reaction, viz. acetalization, can be envisaged. The contribution of this side reaction can be appreciable because it brings about the formation of a stable five-membered ring as shown in Scheme 1.

Indeed, sometimes an exothermic reaction was observed during several copolymerization attempts, but no polymer was produced.

Fig. 1 shows the ^{1}H NMR spectrum of a 1:4 (mol.) VCA–EMVE mixture heated at 60°C for 24 h. The strong signal at 1.2–1.3 ppm attributable to methyl groups in 2-methyl-1,3-dioxolane confirms the formation of cyclic acetal 1 (Scheme 1). Vinylene carbonate may well facilitate the acetalization reaction: it could be partially hydrolyzed by traces of water to form intermediate semiesters of carbonic acid that could catalyze acetalization of EMVE.



Scheme 1.

Because of the side reactions discussed above, the yield of copolymers of VCA and EMVE was substantially lower compared to that of DMVE or TMVE copolymers. In other words, ethylene glycol monovinyl ether is not an appropriate comonomer for VCA owing to several side reactions occurring concurrently.

As can be seen from Table 1, the copolymerization of EMVE and VCA at low concentrations of the initiator yielded products soluble in polar organic solvents (e.g. acetone and DMF) whereas crosslinked copolymers were produced at higher concentrations of AIBN. On the other hand, the copolymerization of DMVE and VCA only produced crosslinked polymers even at low concentrations of the initiator. Obviously, some chain transfer reactions resulting in the formation of crosslinked products were involved in that case. Nurkeeva et al. [27] had studied chain transfer reactions in the copolymerization of *N*-vinyl-2-pyrrolidone with EMVE and DMVE using a spin-trapping method and found that the rate of abstraction of hydrogen atoms from methylene groups in the pendent oxyethylene moieties is considerably higher than that from methylene groups in the main chain. One could conclude, therefore, that the chain transfer reactions mainly occurred at the methylene groups of pendent moieties. The authors, however, could not determine the exact positions of the hydrogen abstraction in the (di)ethylene glycol pendents.

We have also found that copolymerization of VCA and MTVE only produced a linear polymer as is seen from Table 1. This fact may imply that no chain transfer reactions were involved in that case. Therefore, it was reasonable to conclude that the chain transfer reaction predominantly occurs at the methylene groups adjacent to hydroxyl groups of the EMVE or DMVE monomer links (Scheme 2).

In principle, both oxyethylene (i.e. $-OCH_2CH_2-$) and hydroxyl (i.e. $-OH$) moieties are electron-donating groups. However, in the case of the copolymerization of EMVE (or DMVE) with VCA in a 1:1 molar ratio, the hydroxyl groups

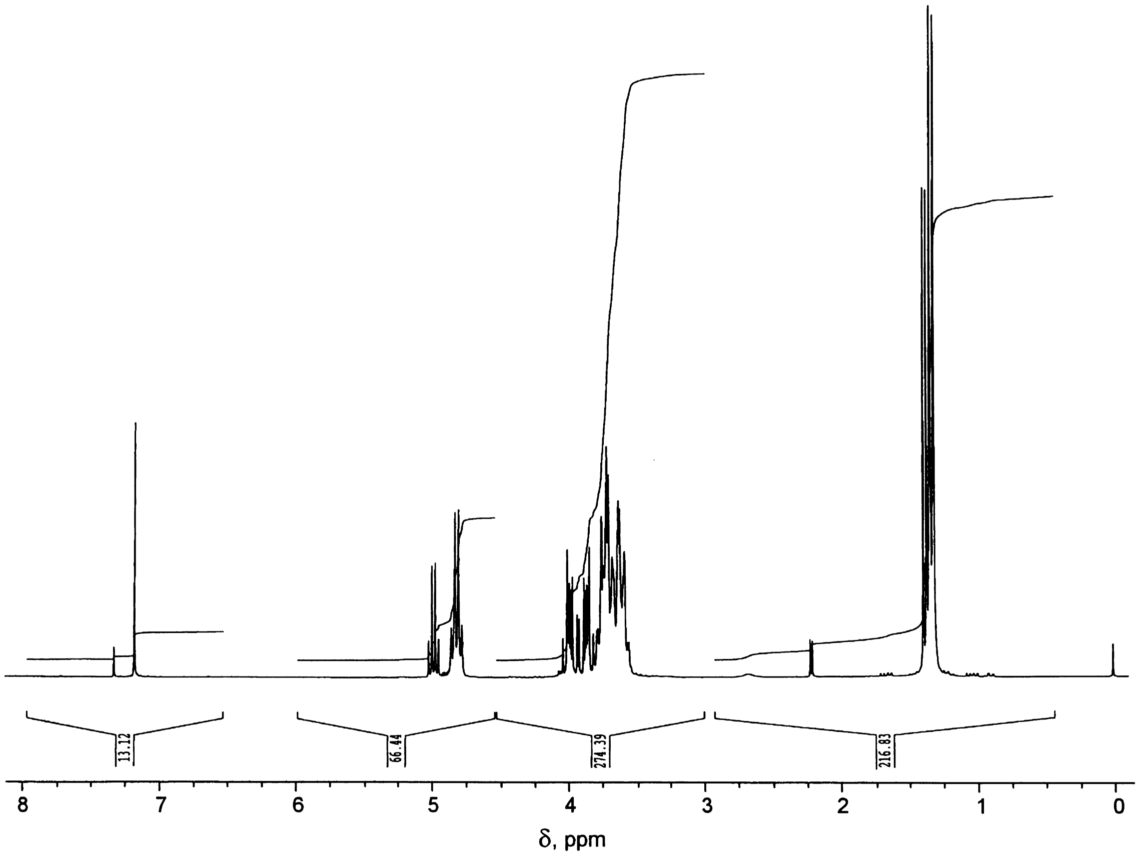


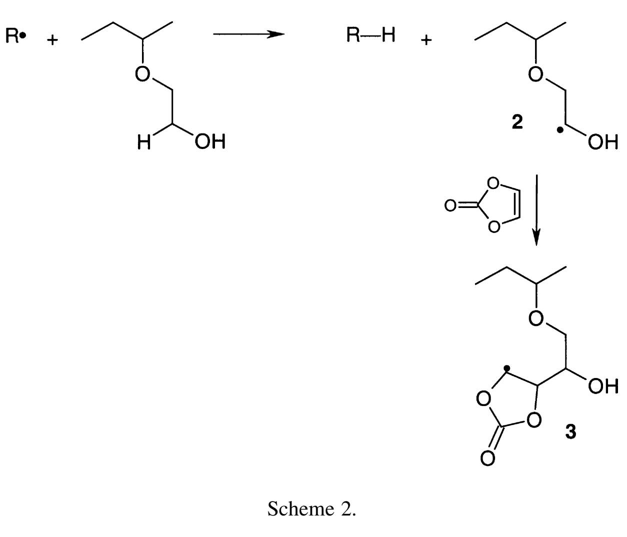
Fig. 1. ^{1}H NMR spectrum of a 1:4 (mol.) VCA–EMVE mixture heated at 60°C for 24 h without radical initiator.

of vinyl ethers might be transformed into weak electron-withdrawing groups due to hydrogen bonding [27] with cyclic carbonate groups as shown in Scheme 3, which could facilitate the formation of radicals **2** in Scheme 2.

It should be noted that the products of alkaline hydrolysis[2] of the crosslinked VCA–EMVE (or DMVE) copolymers were observed to easily decompose under acidic conditions (e.g. in an aqueous 1 M HCl solution) and yield completely soluble fragments (Table 2). This phenomenon can be explained by the presence of a significant proportion of structure **4** (Scheme 4) derived from polyradical **3** (Scheme 2) due to the chain transfer reactions. The hydrolysis of structure **4** can give rise to the formation of vicinal polyol **5** that appears to be unstable under acidic conditions and decomposes due to attack by a proton at the adjacent ether bond as shown in Scheme 4.

Generally, all hydrogels based on copolymers of hydroxyl-terminated oligo(ethylene glycol) vinyl ethers with VCA can contain fragments analogous to structure **5**. It should be noted, however, that in addition to the intermolecular chain transfer reactions (Scheme 2), some intramolecular chain transfer could also be involved in the overall copolymerization route in the case of EMVE and DMVE as shown in Scheme 5.

Thus the copolymerization of VCA with EMVE or DMVE can involve more chain transfer reactions, which can further give rise to the formation of the structure **5** in Scheme 4. According to Nurkeeva et al. [27], the elimination of hydrogen atoms from EMVE links occurs much easier compared to that from DMVE links. This conclusion was supported in our study by the increased stability of hydrolyzed DMVE copolymers under acidic conditions.



Scheme 2.

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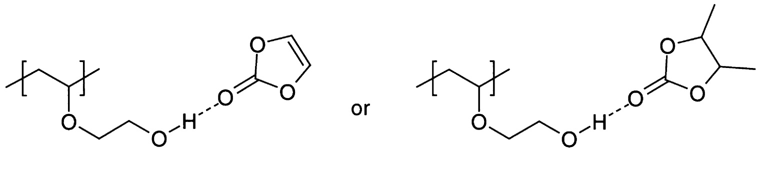
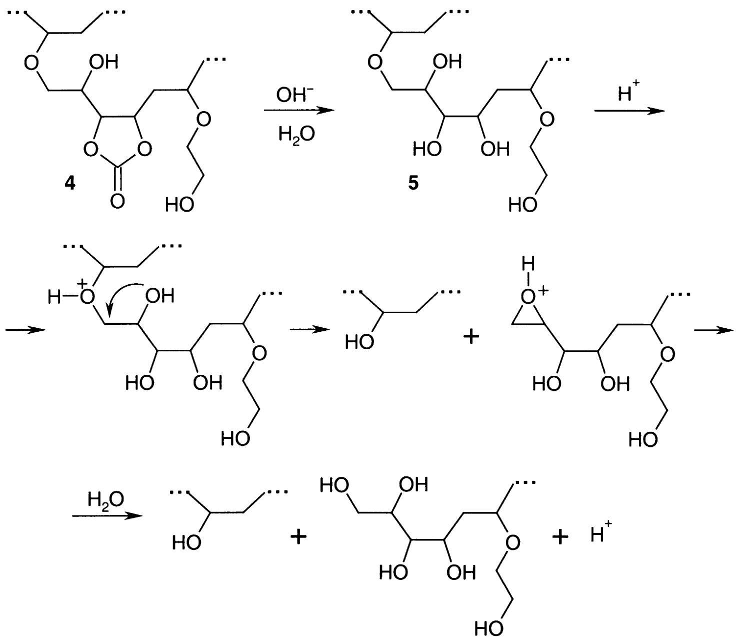
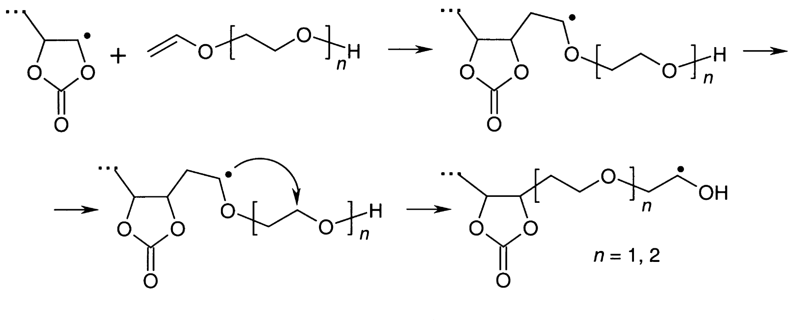
[2] With a 5% aqueous NaOH solution.



Scheme 3.

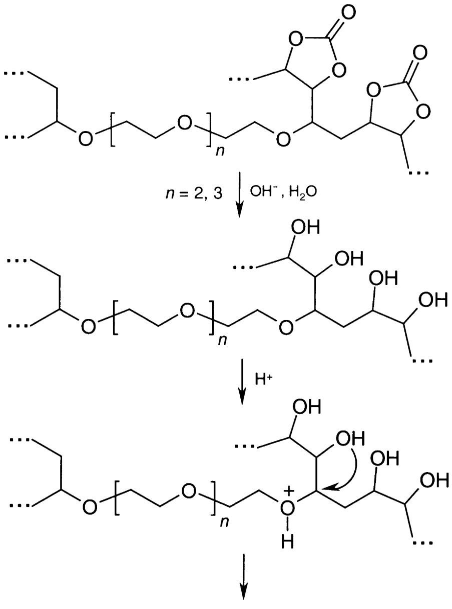


Scheme 4.



Scheme 5.

Table 2 shows that hydrolyzed EMVE–VCA copolymers, even those containing crosslinking agent (i.e. DDVE), still could dissolve in acidic solutions whereas hydrolyzed gels based on the DMVE–VCA copolymers crosslinked by TDVE retained their swellability, although their swelling degree increased. At the same time, the swelling capacity of hydrogels based on the MTVE–VCA copolymers only slightly increased during soaking in acidic solutions for one week, thus suggesting that slow hydrolysis of the network may also occur. Indeed, the gels based on poly(MTVE–VCA) can also upon hydrolysis form acid-cleavable moieties similar to structure **5** (Scheme 4), as shown in Scheme 6. However, the amount of such fragments is small because of the lack of the chain transfer reactions. These facts suggest that copoly(DMVE/VCA) and copoly(MTVE/VCA) crosslinked by oligoglycol divinyl ethers, although partially hydrolyzable under acidic conditions, cannot be destroyed as easily as copoly(EMVE/VCA). Obviously, the difference can be accounted for by a significantly lower contribution (or almost absence in the case of MTVE) of the chain transfer reactions resulting in the formation of hydrolytically unstable fragments in the copolymerization of VCA with DMVE or MTVE as compared to the VCA–EMVE copolymerization.



Scheme 6.

Fig. 2 shows ^{1}H NMR spectra of poly(vinylene carbonate) (PVCA) and MTVE–VCA copolymer. The spectrum of the VCA homopolymer only exhibits a broad signal at δ 5.2–5.7 ppm (curve (1)) whereas in the spectrum of the MTVE–VCA copolymer the signal of cyclic carbonate groups has been shifted upfield to δ 4.4–5.1 ppm (curve (2)). This implies that the electronegativity of the ethylene link in cyclic carbonate moieties has been reduced, presumably, due to the presence of electron-donating substituents, i.e. MTVE monomeric links. One could expect such an effect to occur in the case of the formation of an alternating MTVA–VCA copolymer. Furthermore, based on the NMR spectra, the molar ratio of the monomers in the copolymers was estimated to be 1:1. Since the low tendency of MTVE to homopolymerize can be neglected, one can suggest that the comonomers tend to alternate in the macromolecular chains. In other words, the NMR spectroscopic data indicate the formation of alternating copolymers during the copolymerization of VCA with oligo(ethylene glycol) vinyl ethers.

Fig. 3 shows the FTIR spectra of copoly(DMVE/VCA) and the product of its alkaline hydrolysis. The strong absorption band at 1817 cm^{-1} attributable to cyclic carbonate groups in the spectrum of copoly(DMVE/VCA) (Fig. 3, curve a) completely disappears in the spectrum of the hydrolyzed product (Fig. 3, curve b). This fact indicates that all cyclic carbonate groups in original copoly(DMVE/VCA) were hydrolyzed by treating with an aqueous 5% NaOH solution. As a result, the DMVE–VCA copolymer, whose hydrophilicity was rather moderate, had been transformed into hydrophilic, water-swellable material.

3.2. Swelling behavior of hydrogels based on VCA–OGVE copolymers

The conditions of the copolymerization of VCA with vinyl ethers and degrees of swelling in water of their hydrolyzed copolymers are presented in Table 3. It can be seen that with increasing amount of divinyl ethers, the swelling capacity of the hydrogels markedly decreased, obviously, due to an increased degree of crosslinking (i.e. network density). Since the copolymerization of VCA with both EMVE and DMVE brings about the formation of crosslinked products even without adding any crosslinking agents, the swelling degree of such crosslinker-free hydrogels can probably be considered as the maximum

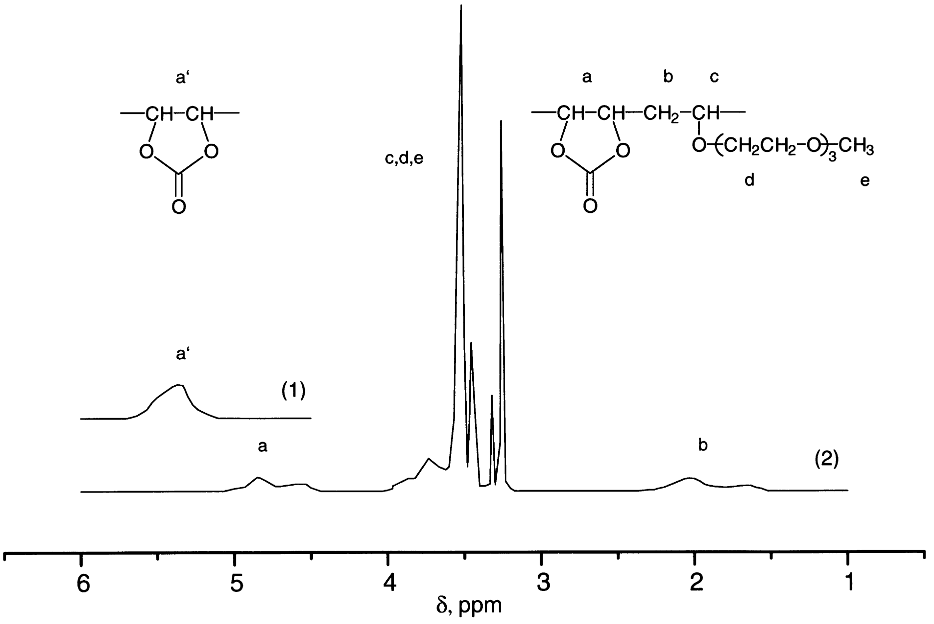


Fig. 2. ^{1}H NMR spectra of PVCA (1) and MTVE–VCA copolymer (2).

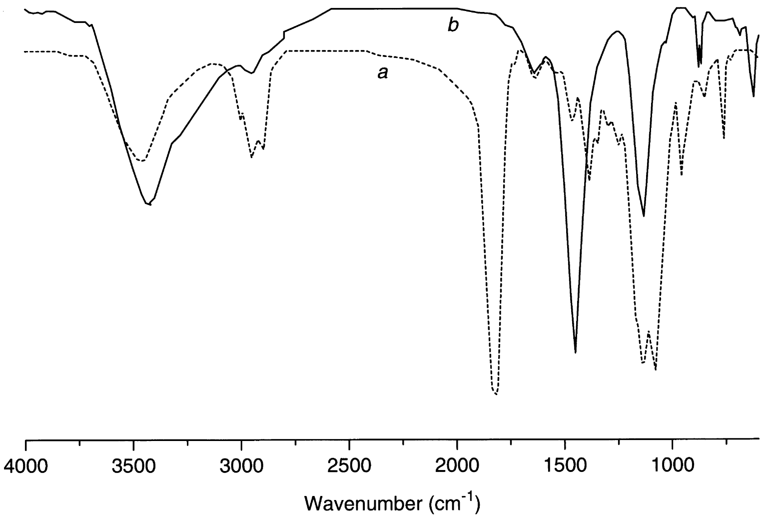


Fig. 3. FTIR spectra of the VCA–DMVE copolymer (a) and the product of its alkaline hydrolysis (b).

swellability of corresponding copolymers produced by bulk polymerization.

On the other hand, no chain transfer reactions were observed in the case of the copolymerization of VCA with MTVE. Therefore, the maximum swellability of hydrogels based on copoly(MTVE/VCA) could be reached by controlling the amount of the crosslinker (TDVE). However, the lowest (optimum) concentration of TDVE was found to be about 1 wt.% (Table 3). At still lower concentrations of the crosslinker, the hydrolyzed copolymers were either soluble in water or much too fragile and therefore difficult to handle in a swollen state.

Generally, the ionic hydrogels, which are capable of electrolytic dissociation, exhibit very high swelling capacities in pure water owing to the repulsion effect between the same electrostatic charges on the polymer network (for a recent review, see Ref. [28]). Unfortunately, aqueous solutions of electrolyte salts, acids or bases can easily shield the charges on the network thus leading to a dramatic shrinkage or even collapse of the hydrogels. On the contrary, nonionic networks, although not possessing that enormous swellability as ionic hydrogels, can show stable swelling behavior in aqueous solutions of various salts due to a lack of ionic groups in their structure. The data presented in Table 4 and Fig. 4 demonstrate that the swellability of all three types of hydrogels based on VCA–OGVE copolymers depends on neither concentration nor type of the electrolyte tested.

However, the data of Table 2 show the hydrogels based on copoly(EMVE/VCA) and copoly(DMVE/VCA) to be unstable under acidic conditions. Those hydrogels (E-2, D-1) decomposed even in weakly acidic (pH 4.0) aqueous solutions to produce completely soluble products. On the other hand, the swellability of hydrogels based on

Table 3

Swellability in water of hydrolyzed copolymers of VCA and oligo(ethylene glycol) vinyl ethers. (Synthesized by copolymerization at 60°C for 18 h)

Sample no.		Vinyl ether (g)	VCA (g)	Crosslinker (g)	AIBN (g)	Yield (%)	S_{wt} (g/g)
E-1	EMVE	2.60	2.40	0.0091	0.040	59	21.1
E-2		2.60	2.40	0.0219	0.040	62	19.8
E-3		2.60	2.40	0.0580	0.040	61	11.4
E-4		2.60	2.40	0.1053	0.040	65	10.8
D-1	DMVE	3.10	1.90	0	0.030	89	21.0
D-2		3.10	1.90	0.0172	0.030	94	18.4
D-3		3.10	1.90	0.0250	0.030	92	11.9
D-4		3.10	1.90	0.0485	0.030	93	11.6
D-5		3.10	1.90	0.0757	0.030	94	8.1
D-6		3.10	1.90	0.0245[a]	0.030	92	16.9
M-1	MTVE[a]	3.50	1.50	0.0537	0.050	89	29.0
M-2		3.50	1.50	0.1125	0.050	91	13.6
M-3		3.50	1.50	0.1524	0.050	95	11.4
M-4		3.50	1.50	0.1923	0.050	93	9.0

[a] TDVE was used as a crosslinker, while DDVE was used in all other runs.

Table 4
Swelling degrees (g/g) of hydrolyzed copolymers of VCA and oligo-(ethylene glycol) vinyl ethers in aqueous 1 M solutions of various salts

Gel[a]	Salt						
	$CaCl_2$	LiCl	KCl	NH_4Cl	$N(CH_3)_3BzCl$	Na_2SO_4	NaAc[b]
E-1	19.2	19.0	18.0	18.1	18.7	18.4	18.6
D-1	22.5	23.0	22.1	21.9	23.3	22.0	20.5
M-1	29.6	29.5	29.4	29.6	28.9	30.0	29.9

[a] See Table 3 for details.
[b] Sodium acetate.

copoly-(MTVE/VCA) depended only slightly on pH, which has been discussed above.

3.3. Thermal behavior of the VCA–OGVE copolymers

The thermal behavior of the copolymers of VCA with oligo(ethylene glycol) vinyl ethers and their hydrolyzed products was studied using differential scanning calorimetry (DSC). The glass transition temperatures (T_g) observed in all VCA–OGVE copolymers and in the homopolymer of VCA (PVCA) are presented in Table 5.

The T_g values in the copolymers, especially in copoly-(DMVE/VCA) and copoly(MTVE/VCA) bearing longer oligoether side chains, were found to be drastically lower as compared to that in PVCA. Surprisingly, the glass transition temperature in copoly(DMVE/VCA) was lower than that in copoly(MTVE/VCA). The lower T_g in the DMVE–VCA copolymer is explained by the flexible ether links in the main polymer backbone resulting from the intramolecular chain transfer reactions as is shown in Scheme 5. The T_g of copoly(EMVE/VCA) was found to be higher than the T_g of its hydrolysis product, which might imply a predominating contribution of cyclic carbonate groups to the overall glass transition temperature. On the other hand, the T_g values of both copoly(DMVE/VCA) and copoly-(MTVE/VCA) were lower than the T_gs of their hydrolyzed products. Presumably, this can be explained

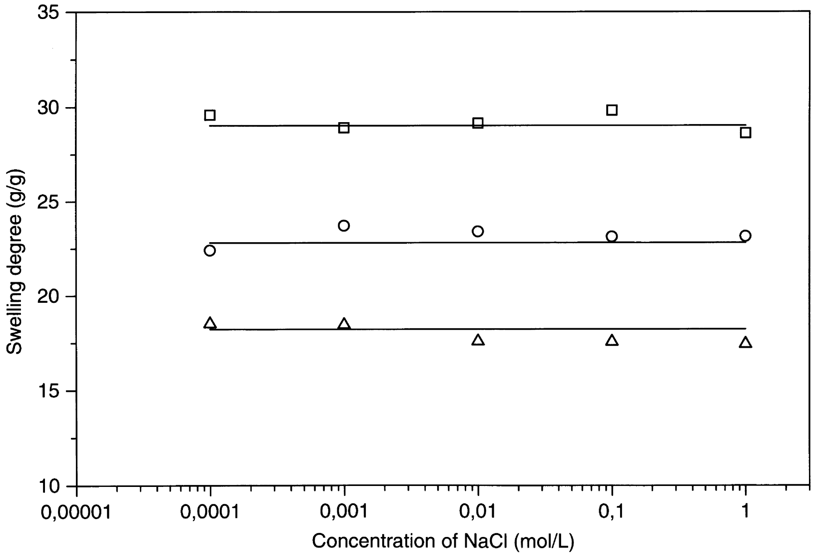


Fig. 4. Swelling degree (g/g) of hydrolyzed copolymers of VCA and oligo(ethylene glycol) vinyl ethers versus the concentration of an aqueous NaCl solution. △ M-1; □ D-1; and ○ E-1 gels (see Table 3 for details).

Table 5
Glass transition temperature of copolymers of oligo(ethylene glycol) vinyl ethers and VCA

Polymer	CP(EMVE/VCA)		CP(DMVE/VCA)		CP(MTVE/VCA)		PVCA
	Original	Hydrolyzed	Original	Hydrolyzed	Original	Hydrolyzed	
T_g^1 (°C)[a]	35	37	− 67	− 43/− 10[b]	− 58/− 19[b]	− 33	–
T_g^2 (°C)[c]	68[d]	40[e]	–	–	–	–	154[d]

[a] Glass transition temperature measured in the first run after cooling the sample from room temperature.
[b] Two glass transitions observed could be accounted for by local inhomogeneities in chemical networks.
[c] Glass transition temperature measured in the second run.
[d] Samples were cooled from 160°C.
[e] The sample was cooled from 80°C.

by the contribution of longer oligoether side chains to the glass transition temperature of those copolymers and by intermolecular hydrogen bonds formed in them after hydrolysis, which could increase rigidity of the ultimate gels.

The difference between the T_g values measured in the first and the second runs can be explained by traces of water still present in the original samples.

4. Conclusions

Three different hydrophilic oligo(ethylene glycol) vinyl ethers were copolymerized with VCA in the bulk. Compared to DMVE and MTVE, EMVE was found to be an inappropriate comonomer because of the side acetalization reaction that caused low yields in the copolymerization with VCA. The copolymerization of MTVE with VCA at a 1:1 molar monomer ratio was found to produce linear alternating copolymers. On the contrary, the copolymerization of EMVE and DMVE with VCA brought about the formation of crosslinked copolymers due to chain transfer reactions occurring at the methylene groups adjacent to hydroxyls in the oligo(ethylene glycol) pendent moieties.

The hydrogels produced by alkaline hydrolysis of the copolymers have been shown to be insensitive to the presence of various electrolytes in aqueous solutions. However, two of them were found to be unstable under acidic conditions. At low pH, the gels based on copoly-(EMVE/VCA) and copoly(DMVE/VCA) decomposed to form water-soluble fragments. In contrast, the hydrogels based on copoly(MTVE/VCE) were found to be relatively stable, and their swellability only exhibited a slight pH dependence. The reason for the acid-sensitivity of the former two gels can be a high proportion of acid-cleavable structural links resulted from the radical chain transfer reactions during the copolymerization of EMVE and DMVE with VCA.

The DSC measurements have shown that the copolymers bearing longer flexible oligoether side chains possess lower glass transition temperatures.

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