Polymer Bulletin 58, 127–138 (2007)
DOI 10.1007/s00289-006-0636-x

Polymer Bulletin

Unusual case of network polymer formation in anionic polymerization of monofunctional vinyl monomer

Boris A. Rozenberg

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka Moscow region, 142432, Russia
E-mail: rozen@icp.ac.ru

Received: 15 July 2005 / Revised version: 10 December 2005 / Accepted: 20 January 2006

Summary

Monofunctional monomers such as hydroxyalkyl (meth)acrylates can form crosslinked polymer in anionic polymerization. This unusual phenomenon relates to a plural reactivity of such type of monomers and their ability to be polymerized by the Michael addition mechanism with the formation of isomerized heterochain fragments of backbone as well as by anionic polymerization with the formation of carbon chain fragments of the main chain. This combination of reaction mechanisms results in the formation of highly branched polymer. Besides these reactions, simultaneous anionic polymerization of hydroxyalkyl (meth)acrylates, an intensive interchain exchange reaction leading to redistribution of the end functional groups and formation of polyester-ether di(meth)acrylate macromolecules result in crosslinking of the generated polymer.

Introduction

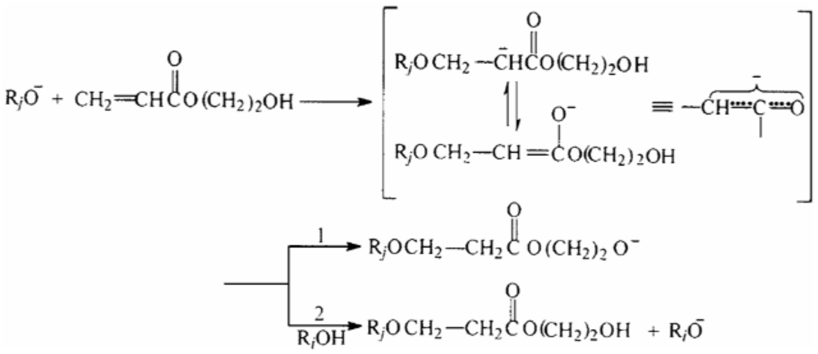
Generally, anionic polymerization of vinyl monomers bearing labile hydrogen atom yields macromolecules with backbone isomerized through Michael addition reaction [1-4]. An alkoxide anion formed in interaction of any anionic initiator with hydroxy group of monomer such as hydroxyalkyl (meth)acrylates by addition to a double bond [5-7] results in tautomeric transformations of initially generated carbanion into a much more stable enolate anion due to its conjugation with a strong electron-acceptor carbonyl group. The existence of hydrogen atom linked to a heteroatom ensures inter- and/or intramolecular reactions of proton transfer to the initially formed carbanion in each elementary event of chain propagation. As a result, isomerization of the backbone takes place and, eventually, hetero chain (polyester type) polymers arise (Scheme 1).

The presence of hydroxy group in the monomer molecule plays a key role in the formation of heterochain polymer in anionic polymerization of the vinyl monomer because of a high rate of proton transfer reaction [4-10]. As expected, in the absence of hydroxy group, anionic polymerization of acrylic monomers with protected hydroxy groups leads to the formation of carbon chain polymers. Recently, Nagasaki

---

Presented at 44th P.M.M. Microsymposium “Polymer Gels and Networks”,
Prague, 10–14 July 2005

et al. [11] reported that potassium ethoxide can initiate the anionic polymerization of 2-(*tert*-butyldimethylsilyloxy)ethyl methacrylate and 2-(diethylamino)ethyl methacrylate in THF [12]. Armes et al [13,14] have performed anionic polymerization initiated by alcoholates of some other tertiary amine methacrylate monomers. Chinese chemists [15] reported this year on successful copolymerization of the above mentioned acrylic monomers under analogous conditions with the formation of highly branched copolymers. Recently, we described the formation of highly branched polymers in anionic polymerization of hydroxyalkyl (meth)acrylates [16, 17].
The present paper is an extension of this approach describing the mechanism of crosslinked polymer formation in anionic polymerization of 2-hydroxyethyl methacrylate (HEMA).



Scheme 1. Michael addition polymerization of 2-hydroxyethyl acrylate (HEA). Hereinafter, for the sake of simplicity, active species are denoted as free anions.

Experimental

Materials

Purification of monomers: HEA and HEMA, and their physicochemical characteristics were previously described in [4]. Metallic sodium and potassium and lithium *tert*-butylate were used as anionic initiators. To prepare the alcoholate, lithium was dissolved in boiling anhydrous alcohol under dry argon. After the alcohol was distilled off, solid alcoholate was isolated in a quantitative yield.

Instruments

The reaction kinetics was studied by isothermal calorimetry using a DAK-1-1 thermal analyzer. Oligomers were studied by exclusion and liquid chromatography on a Waters liquid chromatograph equipped with refractometric and UV detectors. In gel-permeation chromatographic (GPC) measurements, a set of two Separon C18 (250×4 mm) columns was used, which provided a linear calibration in the range of molecular weights from 200 to 5×10^{-5}. GPC measurements were made at a column temperature of 25°C with the use of optically pure THF; the elution rate was 0.3 ml/min. The molecular weights of polymers were calculated from GPC data using calibration plots described in [4].
In liquid chromatographic analysis under critical conditions, a column (150×4 mm) packed with a Silasorb 600 sorbent was used. The column temperature was 60°C, and

the elution rate was 0.7 ml/min. A mixture of methyl ethyl ketone and dioxane (both of chromatographic grade, 4:1 vol/vol) was used as an eluent. The functionality type distribution (FTD) was assessed using the Millennium 32 program.

^{1}H and ^{13}C NMR spectra were measured on a Bruker AC 200-P spectrometer operated at 200 and 50 MHz, respectively. The spectra were taken at 20°C with accumulation of signals (600 cycles). Measurements were carried out using saturated solutions of the tested compounds in deuterated chloroform. All procedures of solution preparation and their filtration, as well as loading of NMR ampoules, were performed in a dry box under argon. The spectra were interpreted using reference data, spectra of individual compounds, and double-resonance techniques.

IR spectra were recorded on a Specord IR-80 spectrophotometer in the 4000-400 cm^{-1} range with drops placed between KBr plates or dry pyridine solutions. The concentration of hydroxy groups was quantified by measuring changes in the intensity of the 3200-3600-cm^{-1} band both in a squeezed drop and in a pyridine solution. The concentration of unsaturated groups was calculated from the intensity of the absorption band at 812 cm^{-1}, corresponding to bending vibrations of CH bonds in $CH=CH_2$ groups. The molar absorption coefficient of OH groups was determined from the calibration curve plotting the intensity or areas under the absorption peaks due to OH groups versus the concentration of *tert*-butyl alcohol and ethanol in pyridine. Absorption bands at 2885 and 1450 cm^{-1}, corresponding to the stretching and bending vibrations of CH bonds in CH_2 groups, respectively, or the absorption band at 1735 cm^{-1} due to carbonyl groups were used as internal standards.

Glass transition temperatures of polymers were measured by TMA using a UIP-70 instrument and DSC on a Mettler-Toledo 822e DSC thermal analyzer.

Polymerization

Polymerization was carried out in a glass reactor equipped with a heated water jacket, stirrer, vacuum line, and line filled with oxygen-free argon. The solid initiator was added or in the form of a *tert*-butyl alcohol solution. 2,2,6,6-Tetramethylpiperidin-l-yloxyl (0.01%-wt) was added to monomers in order to suppress thermally-induced radical polymerization. When the polymerization was complete, the reaction mixture was dissolved in methylene chloride and the growing active centers were neutralized. To this end, the reaction solution was treated with an equivalent amount of the saturated aqueous solution of potassium hydrogensulfate until the reaction of the organic layer was neutral. After separation of the organic layer and drying over anhydrous magnesium sulfate to remove residual moisture, magnesium sulfate was filtered off or decanted. The solid phase was washed with methylene chloride, and the CH_2Cl_2 was combined with the filtrate. The solvent was removed, and the reaction product was analyzed for the content of unreacted double bonds and hydroxy groups by IR spectroscopy and chemical analysis of functional groups [4]. In several experiments, the active growing centers were neutralized by adding an equivalent amount of glacial acetic acid, followed by filtration of its salt.

Results and discussion

The polymerization of HEA and HEMA initiated with alkali metals was carried out in bulk or in THF solutions at temperatures that were several degrees higher than the melting temperature of the metal used. The dissolution of the metal in the reaction mixture under intense stirring occurred within 10-15 min; the color of the reaction system changed to light brown. Potassium turned out to be particularly useful, since it easily dissolved in monomer at the boiling temperature of THF.

Potassium-initiated polymerization of HEMA took place at 100°C under homogeneous conditions after dissolution of the metal. At the moment of potassium dissolution, 13% of double bonds were consumed in the reaction system. Figure 1 shows the kinetics of heat release in the anionic polymerization of HEMA with regard to the potassium dissolution. The polymerization proceeds at the maximum rate with the effective chain growth constant $k = 2.3 \cdot 10^5 \exp(-35.4/RT)$ [l/mol s] [6-8].

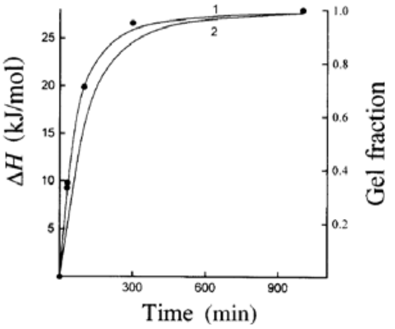


Figure 1. Kinetic curves of heat release in HEMA polymerization initiated with potassium ($[I]_0/[M]_0$ = 0.128 mol/mol) at 100°C (1) and 80°C (2). Dots show part of the gel fraction in the formed polymer at 100°C (right axis).

The HEMA polymerization at 100°C results in a crosslinked rubber-like polymer with a glass transition temperature of 13°C. This polymer is insoluble in methylene chloride, THF, and boiling DMF. At the same time, when HEMA was polymerized at 80°C, a completely soluble polymer was formed. There is no crosslinking in HEA polymerization [15].

The kinetic curve for the consumption of double bonds in the course of polymerization virtually coincides with the kinetic curve for the accumulation of gel fraction in the polymerizing system (Fig. 1). The gel fraction content was determined as a proportion of the polymer insoluble in boiling DMF.

The proportion of the crosslinked polymer significantly decreased as the temperature of polymerization was decreased and the process was carried out in solution. In the latter case, the crosslinked polymer can be absent. The reasons for crosslinking in anionic polymerization of HEMA and a strong temperature dependence of this reaction will be discussed later.

Alkaline hydrolysis of the rubber-like polymer brought about its complete dissolution in water. The aqueous solution was neutralized and the hydrolysis products were extracted with methylene chloride. After drying over anhydrous magnesium sulfate and removing the solvent in vacuum the obtained solution in deuterated chloroform was analyzed by ^{1}H and ^{13}C NMR spectroscopy.

As is evident from the analysis of ^{1}H and ^{13}C NMR spectra of the produced oligomer, the process yields the structures of two kinds, one of which corresponds to the heterochain polymer, and the other to the carbon chain polymer. The contribution of each of the structures can be estimated by measuring directly the fractions of quaternary (a singlet with δ_c=46.8 ppm) and tertiary (a doublet with δ_c= 35.8 ppm) carbon atoms in ^{13}C NMR spectra. The contents of these structures were found to be virtually equal [6-8].

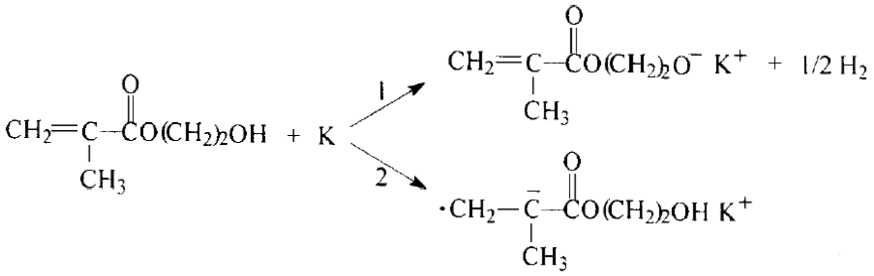
The above experimental results and the data available in the literature [6-8] give us grounds for inferring that the HEMA anionic polymerization involves the following reaction mechanism.

Initiation

Initiation of HEMA and HEA polymerization under the action of alkali metals, as well as under the action of any other anionic initiators mainly proceeds *via* formation of alcoholates (path 1). However, along with this reaction, initiation proceeds also by direct interaction of alkaline metal with double bond with formation of anion-radical (path 2) (Scheme 2) [6–8].

Along with the initiation reaction involving the hydroxy group (path 1), there is a direct interaction of the alkali metal with the double bond of the monomer with formation of an anion-radical (path 2). Herein, we do not discuss in detail the mechanism of further anion-radical transformations which has been the subject of numerous investigations [8]. We can only state for certain that the formation of dimeric anion-radical (the product of monomer addition to the primary anion-radical) with growing anion and radical located at chain ends necessarily occurs along with the reaction of chain growth involving dianion (the product arising from the recombination of primary anion-radicals).

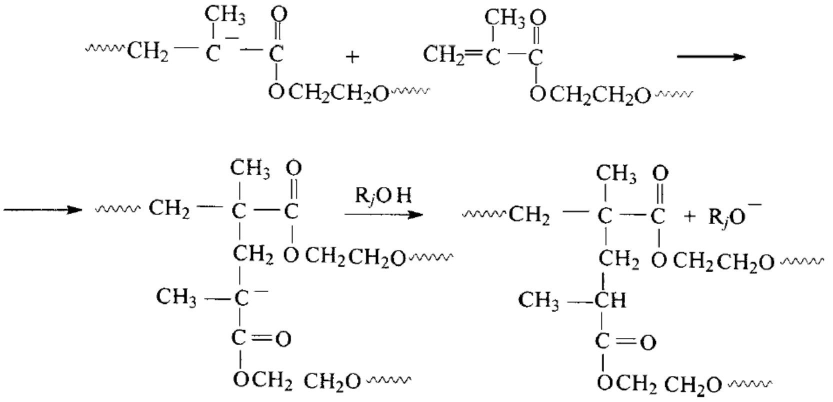
NMR investigation of polyHEMA synthesized by radical polymerization of HEMA [6,7] has shown that there are no repeated quaternary carbon atoms. This implies that contribution of path 2 can be neglected. The validity of this conclusion is also proved by the fact that the radical polymerization is suppressed in the presence of an inhibitor, the nitroxyl radical.



Scheme 2. Mechanism of initiation of HEMA polymerization with potassium.

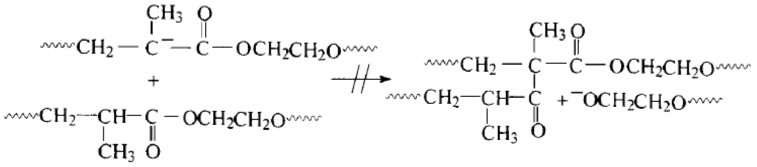
Chain propagation with carbon chain fragments formation

Besides the chain propagation reaction according to Scheme 1, polymerization on the initially generated carbanion with formation of carbon chain fragments takes place in HEMA polymerization initiated with potassium. Let us consider possible pathways for the formation of carbon chain structures in the reaction under examination. As we indicated before, radical polymerization must be rejected. The results of NMR analysis [6,8] unambiguously show that the carbon chain fragments of main chain are produced through the addition of carbanion to the double bond with subsequent transfer of proton from any hydroxy group in the reaction system (Scheme 3).



Scheme 3. The mechanism of carbon chain fragment formation.

The absence in the polymer of ketone groups [6,7] indicates that the formation of carbon chain fragments does not proceed *via* Claisen condensation:



This fact means that the nucleophilic attack of enolate anion on the carbonyl carbon atom of ester group is sterically hindered in comparison with a similar attack on the much more sterically available methylene group of the double bond.

The carbanion results from the addition of a growing alkoxy anion to the double bond or upon the establishment of the acid–base equilibrium between acid and alcoholic groups in the system [6-8].

$$\sim\!\sim CH_2{-}C^-(CH_3){-}C(O){-}OCH_2CH_2O\sim\!\sim + R_jOH \rightleftharpoons$$
$$\sim\!\sim CH_2{-}CH(CH_3){-}C(O){-}OCH_2CH_2O\sim\!\sim + R_jO^-$$

Scheme 4. Acid-base equilibrium in reacting system.

This acid-base equilibrium in the reacting system determines transformation of initially formed hetero chain polymers into the polymer with carbon chain fragments (Scheme 4). In contrast to Michael addition resulting in linear polymer chains, propagation on the growing carbanion affords polymers with branched structure. The nature of the monomer influences to a great extent the topological structure of the polymer formed in anionic polymerization of hydroxyalkyl (meth)acrylates. As expected, the presence of electron-donor methyl group on α-carbon atom of the HEMA double bond results in a much higher content of carbon chain fragments in the generated polymer in comparison with the polymer based on HEA not having such substituent [16]. The polymers generated by anionic polymerization of hydroxy(meth)acrylates are copolymers with highly branched structure because they behave under these conditions not only as AB-monomers but also as AB_2-monomers.

It is worth noting that the nature of counter-ion also affects the topological structure of the generated polymer: the larger the size of counter-ion the higher the carbon chain fragments content [6,7].

Formation of carbon chain fragments is one of the key reactions explaining the formation of crosslinked polymer in HEMA anionic polymerization. Another key reaction responsible for crosslinking in anionic polymerization of HEMA is interchain exchange reaction.

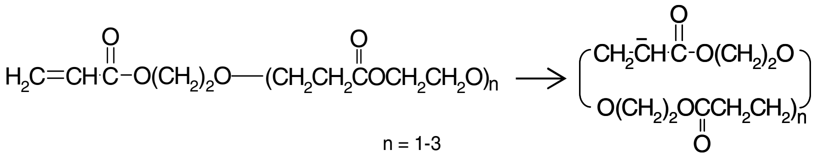
Interchain exchange reaction

Among the obvious side reactions that take place in anionic polymerization of hydroxyalkyl (meth)acrylates are interchain exchange reactions, proceeding *via* a transesterification mechanism. These reactions result in redistribution of macromolecules as regards their length and functional end-groups. Identification of such type of interchain exchange reactions is rather difficult because these reactions do not practically change average characteristics of polymers such as molecular weights, type of backbone, concentration and nature of functional end-groups [18]. That is why the majority of conventional techniques for polymer characterization (IR, UV and NMR spectroscopy, chemical analysis, etc.) do not allow interchain exchange reactions to be identified even qualitatively. At the same time, data on the real composition of macromolecules, i.e., distribution according to functionality types (FTD) of the reacting system, are extremely important, not only from the academic point of view but also from the practical one, for preparation of polymers for specific applications. The FTD data are of particular importance for reactive oligomers, because the FTD affects the properties of related materials.

This problem was solved by HPLC under critical conditions [9,10]. Liquid chromatography under conditions close to critical (the regimes being intermediate of adsorption and exclusion ones) is the most efficient method for analysis of macromolecule distribution according to functionality types. Under critical conditions, retention volumes of macromolecules with a uniform structure of the backbone do not depend on the chain length. Under these conditions, linear macromolecules without strongly adsorbed functional groups elute near the excluded volume. The nature and number of functional groups [19–21] mainly determine retention volumes of functional macromolecules.

The detailed technique for FTD characterization of polymerization products in anionic polymerization of hydroxyethyl (meth)acrylates is described in [9,10]. Using this technique it was found that anionic polymerization of HEA initiated with *tert*-BuOLi yields, in addition to the target product, (macromonomer) macromolecules containing the acrylate groups on both ends (polyester diacrylates) and an equivalent amount of macromolecules with two hydroxy end-groups (polyester diols).

A small amount of macrocycles is formed as well by intramolecular attack of growing alkoxide anion on the double bond of its own chain. It is worth noting that intramolecular transesterification through the attack of propagating species on any ester group of its own molecule does not lead to macrocycles and results in linear chains only, with the same structure of the reaction product as was the initial one. Figure 2 presents a typical chromatogram of the polymer formed in HEA polymerization.



$$H_2C{=}CH\overset{O}{\overset{\|}{C}}{-}O(CH_2)_2O{-}(CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2O)_n \longrightarrow \left(\begin{matrix} CH_2\bar{C}H\overset{O}{\overset{\|}{C}}{-}O(CH_2)_2O \\ O(CH_2)_2O\underset{O}{\underset{\|}{C}}CH_2CH_2 \end{matrix}\right)_n$$

$n = 1\text{-}3$

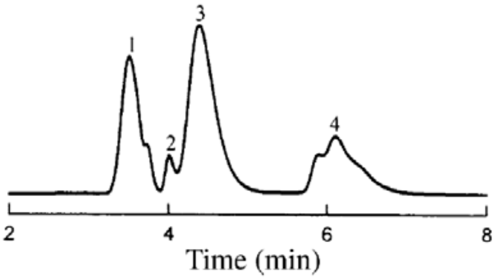


Figure 2. Functional group distribution of a HEA oligomer prepared by HEA polymerization under the action of *tert*-BuOLi. For designation of peaks, see Table 1.

The assumption that the carbon chain polymer arises from the potassium-initiated polymerization of HEMA was convincingly proved by the results of liquid chromatography measurements carried out under the conditions close to critical. Along with the four types of molecules with the heterochain backbone (polyester diacrylates, macrocycles, macromonomers, polyester diols), a fraction that immediately follows the macromonomer appears on the chromatographic curve of the polymer. This fraction is also partially resolved with respect to molecular weight. Figure 3 presents a typical chromatogram of this type.

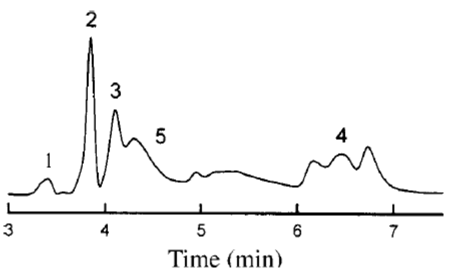


Figure 3. Functional groups distribution of HEMA oligomer derived by HEA polymerization under the action of potassium. For designation of peaks, see Table 1.

The numerical characteristics of molecular weight distribution for the sol fraction of polymers isolated at a conversion of 90% are in Table 1.

It should be emphasized that the polydispersity of the polymer is rather great, thereby indicating the pregel state of the sol. Note that the maximum polydispersity of a purely heterochain polymer does not exceed two.

Table 1. Molecular characteristics of HEA and HEMA oligomers

Reaction conditions	FGD[a]					MWD		
(monomer; initiator; $[M]_0/[I]_0$; T (°C); conversion)	1	2	3	4	5	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
HEA; *t*-BuOLi; 34.0; 20; 0.80	19.5	9.8	48.4	22.3	–	1120	1800	1.61
HEMA; K; 7.8; 70; 0.93	24.5	4.9	12.9	6.3	42.9	1870	5800	3.15

[a] Polyesterdiacrylates (1), macrocycles (2), macromonomers (3), polyesterdiols (4) and polymer with carbon chain fragments (5).

Kinetics of accumulation of all types of macromolecules in the course of HEMA polymerization initiated with potassium and obtained by HPLC under conditions close to critical are presented in Figure 4.

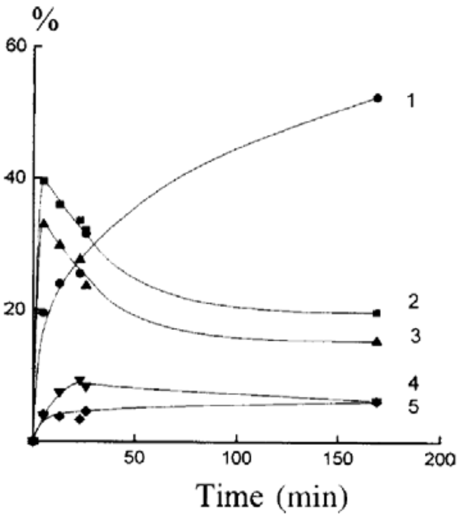


Figure 4. Kinetics of accumulation of macromolecules bearing carbon chain fragments (1), macromonomer (2), polyester dimethacrylate (3), macrocycles (4) and polyester diol (5) in HEMA polymerization under the action of potassium (0.128 mol/mol) at 80°C.

As one can see, all kinetic curves of the formed macromolecules, except for macromolecules with carbon chain fragments are curves with maxima. The fraction of macromolecules with carbon chain fragments progressively increased. Such kinetic behavior means that this type of macromolecules is generated at the expense of macromonomers and polyester di(meth)acrylates as supplier of double bonds for the formation of carbon chain fragments.

Table 2 summarizes some characteristics of the network polymer formed in HEMA polymerization under the action of potassium at 100°C.

Table 2. Characterization of properties and backbone structure of the network polymer formed at HEMA polymerization under the action of potassium at 100°C.

Backbone structure	ΔH of polymerization (kJ/mol)	T_g (°C)	fraction (^{1}H-NMR)	fraction (PDG)
Network polymer	−27.7	13		
Carbon chain[a]	−59.0 (0.42)	77 (0.45)	0.50	0.43
Hetero chain[a]	−7.2 (0.58)	−39 (0.55)	0.50	0.57

[a] Calculated values of ΔH and T_g for the respective backbone structures of HEMA polymers. Calculated fractions of the respective backbone structures are given in parentheses. Other values have been determined experimentally.

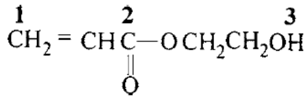
The ratio of hetero-chain and carbon-chain polymers was measured directly by ^{1}H NMR and FTD techniques and calculated using the values of enthalpy of HEMA polymerization under the action of potassium and glass transition temperature, T_g, of the polymer formed and taking into account the additive contributions of both types of the chain structure in the network. The glass transition temperature of network fragments was calculated using the Cheops-4 computer program [22]. The results presented in Table 2 have shown that the methods used are in a good accordance and give an approximately 1:1 molar ratio of hetero- and carbon-chain polymers formed in HEMA polymerization under the action of potassium at 100°C [6,7]. The obtained results unambiguously show that HEMA polymer is a network copolymer composed of hetero and carbon chains.

It is worth noting that the anionic polymerization of HEMA, accompanied by proton transfer in each event of chain growth, affords only linear chains even when dimethacrylates and dianions (or diols in the protonated form) occur in the reaction system. The highly branched and crosslinked polymer can arise from the anionic polymerization of HEMA only when a carbanion appears at the intermediate stage on the addition of a growing alkoxide anion to the double bond, yielding the carbon chain polymer. However, this reaction is suppressed because of a rapid proton transfer to the carbanion. Nevertheless, as conversion grows, i.e., in the course of consumption of hydroxy groups, equilibrium in this reversible acid-base reaction (Scheme 4) gradually shifts to the left-hand side and the role of anionic polymerization affording crosslinked carbon chains increases.

The strong temperature dependence of crosslinking observed in HEMA anionic polymerization is related to high steric hindrance in the carbanion anion reaction with double bond with the formation of carbon chain fragments.

Conclusions

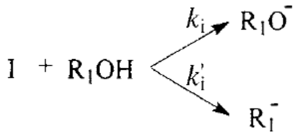
The monomers studied under the conditions of anionic polymerization displayed plural reactivity towards initiating and propagating anions simultaneously at three sites as indicated in the scheme:



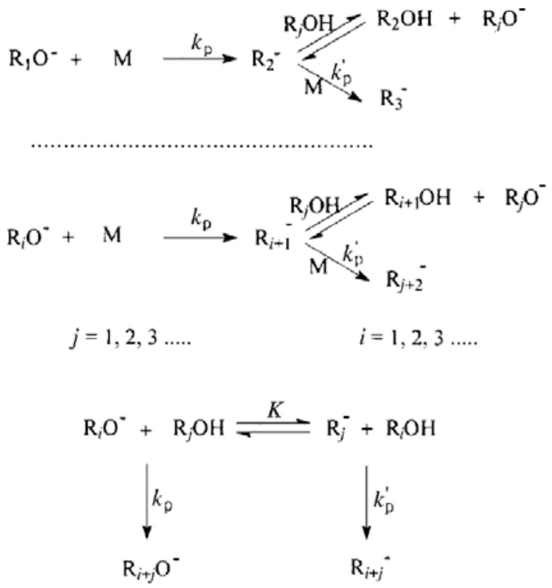
$$\overset{1}{CH_2} = CH\overset{2}{\underset{\underset{O}{\|}}{C}}-OCH_2CH_2\overset{3}{OH}$$

Such plural reactivity defining polymerization mechanism is summarized in the following simplifed kinetic scheme:

Initiation



Chain propagation



Proton transfer

$$R_jO^- + R_iOH \underset{k_{tr2}}{\overset{k_{tr1}}{\rightleftharpoons}} R_iO^- + R_jOH$$

$$k_{tr1} \gg k_p: \qquad K_1 = \frac{k_{tr1}}{k_{tr2}} \sim 1$$

Chain transfer on polymer

$$R_jO^- + R_iOH \overset{k_a}{\rightleftharpoons} (\text{Adduct})^- \underset{K_a \ll 1}{\overset{k_{tr}}{\rightleftharpoons}}$$

$$R_iOCH_2CH_2COOR_{j-k} + {}^-OCH_2CH_2OR_{k-1}OH$$

Here Rj designates j-mer with terminal double bond and R_j^- is carbanion generated by addition of any anion to the double bond or by acid–base equilibrium reaction with equilibrium constant K.

Hydroxyalkyl (meth)acrylates are typical representatives of the derivatives of α,β-unsaturated acids bearing groups with labile hydrogen atom. Under the conditions of anionic polymerization such type of monomers can act as AB* inimer, where A stands for double bond and B* is an initiating site, and can be used for self-condensation vinyl polymerization and/or copolymerization [23,24] with conventional vinyl monomers for preparation of highly branched polymers. Combination of such properties with easy interchain exchange reaction creates unique conditions for formation of crosslinked polymers in HEMA anionic polymerization [6-8] or its copolymerization with conventional vinyl monomers.

Acknowledgements. The research was supported in part by the Russian Foundation for Basic Research (Project 01-03-32674), the Division of Chemistry and Materials Sciences of the Russian Academy of Sciences (Project 04-12-131), and the International Science and Technology Center (Project 02-1918).

References

1. Breslow DS, Hulse GE, Matlack AS (1957) J Am Chem Soc 79:3760
2. Saegusa T, Kobayashi S, Kimura Y (1974) Macromolecules 7:256
3. Saegusa T, Kobayashi S, Kimura Y (1975) Macromolecules 8:950
4. Rozenberg BA, Bogdanova LM, Dzhavadyan EA, Komarov BA, Boiko GN, Gur'eva LL, Estrina GA (2003) Polym Sci 45A:1
5. Rozenberg BA (2003) Int J Plast Technol 6:17
6. Rozenberg BA, Boiko GN, Bogdanova Dzhavadyan EA, Komarov BA,. Kushch PP, Estrina GA (2003) Polym Sci 45A:819
7. Rozenberg BA (2004) Designed Monomers Polym 7:135
8. Rozenberg BA (2003) Macromol Symp 199:443
9. Estrina GA, Komarov BA, Estrin YI, Rozenberg BA (2004) Polym Sci A 46:97
10. Rozenberg BA, Estrin YI, Estrina GA (2004) Int J Polym Anal Charact 9:197
11. Nagasaki Y, Sato Y, Kato M (1997) Macromol Rapid Commun 18:827
12. Lijima M, Nagasaki Y, Kato M, Kataoka K (1997) Polymer 38:1197
13. Lascelles SF, Malet F, Mayada R, Billingham NC, Armes SP (1999) Macromolecules 32:2462
14. Vamvakaki M, Billingham NC, Armes SP (1999) Macromolecules 32:2080
15. Jia Z, Huang W, Yan D (2005) e-Polymers 17:1
16. Rozenberg BA, Irzhak VI, Komarov BA, Estrina GA (2005) Polym Sci A 47:226
17. Rozenberg BA, Boiko GN, Gur'eva LL, Dzhavadyan EA, Komarov BA, Estrina GA (2004) Polym Sci A 46:226
18. Rozenberg BA, Irzhak VI, Enikolopov NS (1975) Interchain Exchange of Polymers. Khimiya, Moscow
19. Entelis SG, Evreinov VV, Kuzaev AI (1985) Reactive Oligomers. Khimiya, Moscow
20. Entelis SG, Evreinov VV, Gorshkov AV (1987) Adv Polym Sci 76:129
21. Berek D (1996) Macromol Symp 10:33
22. Askadskii AA, Kondrashchenko VI (1999) Computer Materials Science. Nauchnyi Mir, Moscow
23. Frechet JMJ, Henmi M, Gitsov I, Aoshima S, Leduk MR, Grubbs RB (1995) Science 269:1080
24. Litvinenko GI, Simon PFW, Muller AHE (2001) Macromolecules 34:2418