Macromol. Symp. **2003**, *199,* 443-453

Vinyl Monomers Containing Active Hydrogen Atoms Are a New Type of Monomer for Polycondensation

Boris A. Rozenberg

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

Summary: The latest findings in author's laboratory devoted to the understanding kinetic peculiarities and mechanism of vinyl macromonomers formation by the example of anionic polymerization of 2-hydroxyethylacrylate (HEA) and 2-hydroxyethylmethacrylate (HEMA) containing group with mobile hydrogen atoms are discussed. It was shown that polymerization is accompanied by proton-transfer in each elementary propagation step, which leads to isomerization of the backbone and formation of polyester type macromonomers. Polymerization is accompanied by side transesterification reaction with formation of polyester diacrylates and polyester diols. The peculiarities of polymerization mechanism under the action of alkali metals and its alkoholates were established. Expected applications of the polymerization products are discussed.

Keywords: 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, macromonomers, proton-transfer anionic polymerization, transesterification reaction

Introduction

Vinyl monomers containing groups with active hydrogen atom like (meth)acrylamides hydroxyalkyl(meth)acrylates, (meth)acryloylalkyl(aryl)urethanes etc. are easily transformed to corresponding heterochain polymers through Michael addition polymerization mechanism under the action of base-type catalysts. For the first time such type of polymer formation was discovered about half a century ago.[1, 2] However, even in the basic work entitled "A Novel Synthesis of Poly-β-alanine from Acrylamide" it was realized that the real mechanism of polymerization is much more complex and it was assumed that one of the propagation steps include a proton transfer reaction. Despite the permanent interest of researchers in such systems[1-12] there is still the obvious lack in understanding kinetic features and mechanism of polymerization and structure of the generated polymers. Brief but practically exhaustive overview of the current status of research on the proton-transfer anionic polymerization of vinyl monomers is given in

DOI: 10.1002/masy.200350937

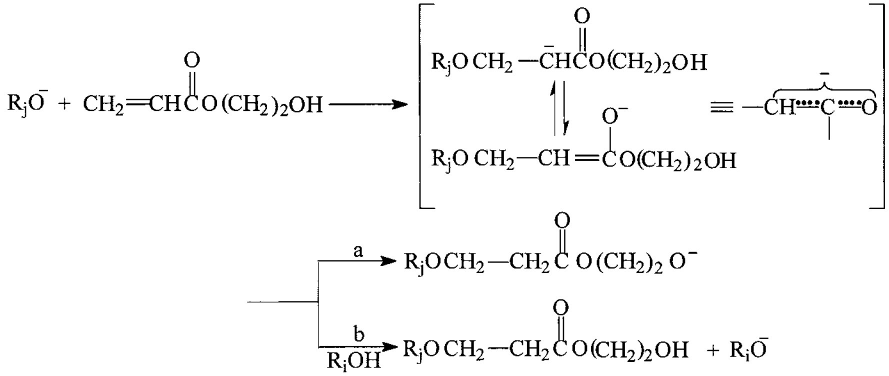
reference.[12] A new wave of interest to proton-transfer anionic polymerization of vinyl monomers appeared at the last time[7-15] as to the promising synthetic technique that allows preparing valuable products for technical and biomedical applications. Proton-transfer anionic polymerization can be used for the preparation of a family of macromonomers with different heterochain backbone and related comb-like, superbranched and crosslinked polymers on the basis of vinyl monomers containing groups with mobile hydrogen atom. Anionic polymerization of such a class of vinyl monomers can introduce functional groups into the main chain of polymers and provide necessary terminal functional groups. The objective of the paper is to shorten a gap in understanding the mechanism of the reactions under study.

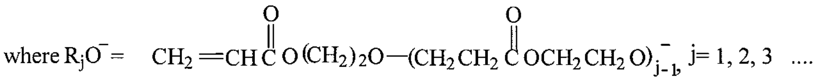
Experimental

Detailed description of HEA and HEMA purification as well as apparatus for polymerization is described in reference.[12] Analytical techniques IR-, ^{1}H and ^{13}C NMR spectroscopy, ESR, HPLC, GPC, DSC and isothermal microcalorimetry, TMA, elemental analysis, chemical analysis of functional groups used for kinetic investigations and structure characterization of generated polymers are described in the same paper.[12] Special attention was paid to characterization of functional group distribution (FGD) on macromolecules. In order to solve this problem a special HPLC technique in conditions close to the critical ones was worked out for the analysis of synthesized polymers.[13]

Results and Discussion

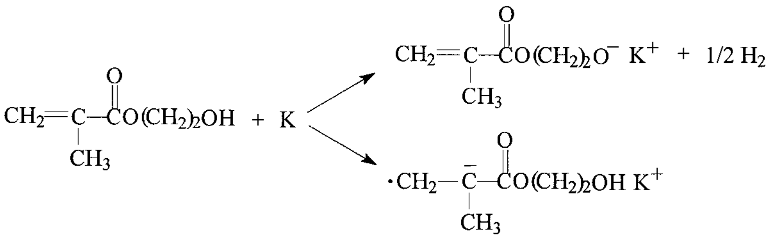
IR- and NMR spectroscopic data unambiguously indicate that HEA and HEMA are undergone step polymerization through Michael addition reaction under the action of alcoholate type propagating centers formed by any anionic initiator.[12] Step polymerization proceeds via anionic polymerization mechanism accompanying by intra- (path a) or intermolecular (path b) proton-transfer on the ester enolate in each elementary propagation step, which leads to isomerization of the backbone and formation of heterochain (polyester type) polymer. Therefore, such type of polymerization can be called not only proton-transfer but also “isomerization” or “heterochain” polymerization contrary to conventional anionic polymerization of (meth)acrylates resulting in carbochain backbone of polymers.





$$\text{where } R_jO^- = CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_2O{-}(CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2O)_{j-1}^-,\ j = 1, 2, 3\ \ldots.$$

Initiation reactions. The structure of the generated polymers in a great extent depends on a type of initiator used. Formation of alkoxy anion as active propagating center at interaction of hydroxyl groups of monomer or macromonomer with anionic initiator is main mechanism of initiation. However, proton-transfer polymerization of HEMA and HEA under the action of alkali metals is accompanied by conventional vinyl polymerization of methacrylate's double bond.



Initiation proceeds with formation of anion-radical, which generates two types of backbone chains (hetero-and carbochain respectively). The final polymers are insoluble in organic solvents and displays network behavior on TMA curve. However, rubbery network polymer based on HEMA is readily dissolved in boiling water due to its alkali hydrolytic decomposition with formation of ethylene glycol, methacrylic, polymethacrylic acids, and 2-hydroxyethyl-β-oxy-α-methylpropionic acids after neutralization, that were identified by ^1H and ^{13}C NMR.[14] The ratio of heterochain and carbochain polymers was measured directly by ^1H NMR and FGD techniques and indirectly calculated using the values of HEMA polymerization enthalpy under the action of potassium and T_g of polymer formed. All methods used are in a good coincidence and give approximately 1:1 molar ratio of hetero- and carbochain polymers formed at HEMA polymerization under the action of potassium at 70-100°C.[14] These polymers are represented a mixture of heterochain homopolymer of HEMA and block copolymer of HEMA with hetero- and carbochain structure of interknot chains.

Addition of inhibitor (2,2,6,6-tetramethyl-N-piperidine oxide) completely suppresses radical polymerization and formation of network polymers. Formation of heterochain polymers is the only result of such inhibited HEMA or HEA anionic polymerization under the action of alkali metals.

Table 1. Characterization of properties and backbone structure of the network polymer formed at HEMA polymerization under the action of potassium.

Backbone structure	ΔH at polymerization kJ/mol	T_g °C	^{1}H NMR fraction	FGD fraction
Network polymer	-27,7	13		
Carbochain [a)]	-59,0 (0,42)	77 (0,45)	0.50	0.43
Heterochain [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 brackets. Other values are experimentally measured

One of the most attractive initiators is t-butanol-based alcoholates. This family of initiators with different counterions contrary to the other alcoholates due to unique combination of high basicity and high spatial hindrance initiates HEA and HEMA polymerization via exchange reaction with hydroxyl group of monomer only. There is no direct addition reaction of this initiator to the double bond of monomer that is revealed by analysis of ^{1}H and ^{13}C NMR data. Well-known fact of impossibility to initiate of MMA polymerization under the action of t-butoxides,[16] and what is more, the fact of successful utilization of t-butoxides as ligands for stability and activity control of initiators and active species at conventional anionic polymerization of MMA[17] also confirm this conclusion.

NMR data indicates proceeding of side reactions through acyl-oxygen and alkyl-oxygen scission in the presence of excess of t-butanol, which sometimes are used as a solvent for t-butoxides. There are no side reactions in the absence of t-butanol.[15]

Chain propagation. Establishment of molecular weight relationship as a function of conversion is a key problem in understanding the mechanism of the chain propagation reactions under study. There are two alternative mechanisms of chain growth: chain polymerization ($R_j + M \rightarrow R_{j+1}$) and step growth polymerization ($R_j + R_i \rightarrow R_{j+i}$) in the systems under study.

Chain growth polymerization mechanism is realized at heterogeneous development of the reaction only when the polymerization products R_jOH with $j \geq 2$ are phase separated due to the growth of hydrophobicity of macromonomer formed at increasing chain length. Step growth polymeryzation must be realized in homogeneous system.

All investigated polymerization systems proceed in bulk heterogeneously. The law for living chain growth polymerization is

$$P_n = \frac{\alpha[M]_0}{[I]_0} = \alpha P_{n,\infty} \qquad (1)$$

where α is conversion of double bonds or hydroxyl groups, $[M]_0$ and $[I]_0$ are initial monomer and initiator concentrations, $\overline{P}_n$ and $\overline{P}_{n,\infty}$ are current and ultimate average polymerization degree, describes satisfactorily our own and literary data[12] for HEA and other hydroxyalkylacrylate polymerizations under the action of different initiators and temperatures. It means that chain growth polymerization mechanism is dominating.

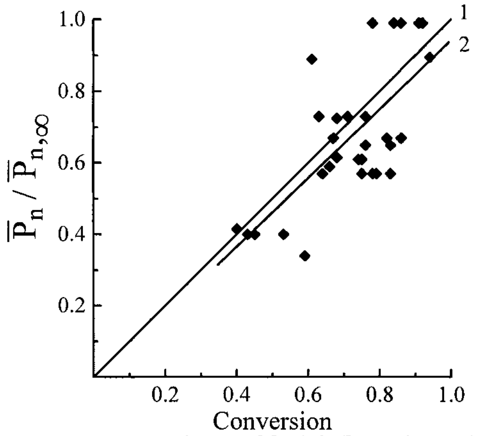


Fig. 1. $\overline{P}_n / \overline{P}_{n,\infty}$ versus conversion at $[I]_0$ / $[M]_0$ ≥ 0.05. 1 is theoretical line, 2 is linear approximation of experimental data.

Fast exchange equilibrium reaction of propagating alkoxyanion with any terminal hydroxyl group of molecules in the absence of termination reactions makes such polymerizing system "living".

$$R_jOH + R_iO^- \rightleftharpoons R_jO^- + R_iOH$$

Essential deviation from living chain growth polymerization are observed at initiator to monomer molar ratio < 0.05 that can be related to partial proceeding of the reaction via step growth polymerization under these conditions.

Secondary and side reactions. The polydispersity of polymer increased in the course of polymerization from 1 and tend to 2 at the end of the reaction because of partial parallel proceeding of step growth polymerization and chain exchange reactions.[12, 18] The latter reaction results in redistribution of terminal groups of macromolecules and formation of polyesterdi(meth)acrylates and polyesterdiols in the reaction system. Such types of macromolecules can be observed directly in the reaction product by adsorption chromatography in the conditions close to the critical one[13] (Fig. 2 and 3).

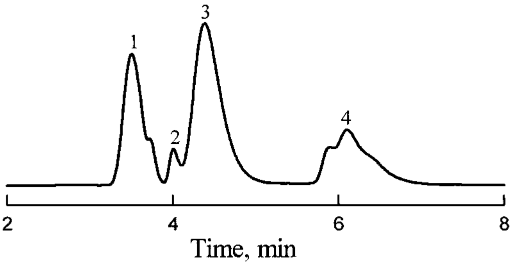


Fig. 2. Functional groups distribution of HEA oligomer produced under the action of BuOLi. Detailed description see in Table 2.Formation of polymers with carbochain backbone is revealed by FGD analysis of polymers produced at HEMA polymerization initiated by alkali metal[13] (Fig. 3).

It is interesting to note that proceeding chain exchange reaction intra-molecularly does not lead to the macrocycles (back-biting cyclization) because the structure of the reaction product is the same as the initial one. Macrocyclization reaction in such systems takes place only when growing alkoxy anion attacks double bond of its own chain.[13] Formation of small cycles is the most probable cyclization reaction.

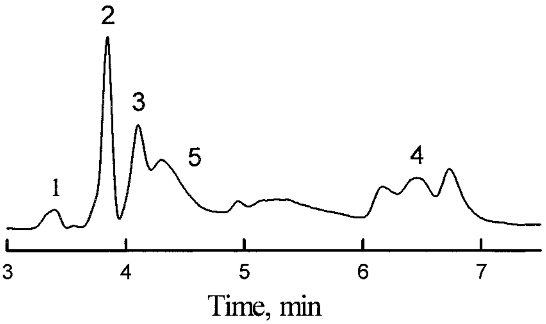


Fig. 3. Functional groups distribution of HEMA oligomer produced under the action of potassium. Detailed description see in Table 2.

Table 2. Molecular characteristics of HEA and HEMA oligomers.

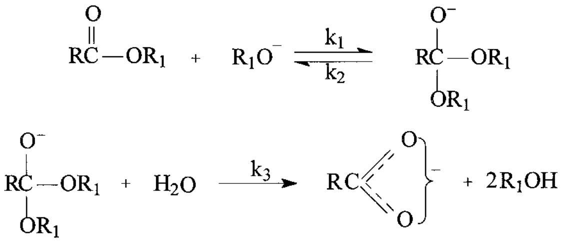
Reaction condition: Monomer; initiator; $[M]_0/[I]_0$; T,°C; conversion	FGD[a)					MWD		
	1	2	3	4	5	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
HEA; t-BuOLi; 34,0; 20; 0,80	19.5	9.8	48.4	22.3	–	1120	1800	1.61
HEMA; K; 7,8; 70; 0,93	24.5	4.9	12.9	6.3	42.9	1870		

a)Polyesterdiacrylates (1), macrocycles (2), macromonomers (3), polyesterdiols (4) and carbochain polymer (5).

As expected, heterochain reaction product is readily undergone crosslinking under the action of radical initiators or UV- irradiation.[12] Alkaline hydrolysis of crosslinked polymer results in formation of ethylenglycol, methacrylic, polymethacrylic, and 2-hydroxyethyl-β-oxy-α-methylpropionic acids that were identified by ^1H and ^{13}C NMR spectroscopy.

Chain exchange reaction proceeds via transesterification mechanism with formation of intermediate adduct. Kinetic study of model reaction of ethylacetate with sodium ethanolate in ethanol solution containing traces of water by IR-spectroscopy gives the possibility to estimate the value of rate constant of intermediate adduct formation that is a limiting stage of chain exchange reaction.[15]

Such model system can be described by the following kinetic scheme:



where R=CH_3, R_1=C_2H_5, k_1, k_2 *u* k_3 are constant rate of the respective reactions.

The rate of ethylacetate (EtOAc) consumption at quasi-stationary approximation on concentration of tetrahedral intermediate reaction product ([Ad]) can be described by the following equation:

$$\frac{d\alpha}{dt} = \frac{k_1 k_3 [EtOAc]_o (1-\alpha\beta)(1-\alpha)[H_2O]}{k_2 + k_3[H_2O]} \qquad (2)$$

where α is conversion of EtOAc equal to $\alpha = ([EtOAc]_o - [EtOAc])/[EtONa]_0$, and $\beta = [EtONa]_o / [EtOAc]_o$. Taking into account that $k_3[H_2O] >> k_2$ solution of this equation gives

$$\frac{\ln(1-\alpha\beta) - \ln(1-\alpha)}{1-\beta} = k_1[EtOAc]_o t, \qquad (3)$$

which quite well describes all kinetic curves at chosen initial conditions (Table 3 and Fig. 4) and the value of k_1=(1,1± 0,1) 10^{-3} l/mol·s determined from initial reaction rate.

Table 3. Rate constant of intermediate adduct formation at transesterification.

№	Reaction condition, T= 25°C				
	[EtOAc]o mol/l	[EtONa]o mol/l	[EtOH]o mol/l	k_1, l/mol·s	
1.	0,089	0,075	16,9	$0{,}93\cdot10^{-3}$	
2.	0,10	0,059	16.9	$1{,}17\cdot10^{-3}$	k_1=$(1{,}1\pm0{,}1)\cdot10^{-3}$
3.	0,119	0,041	16.9	$1{,}17\cdot10^{-3}$	

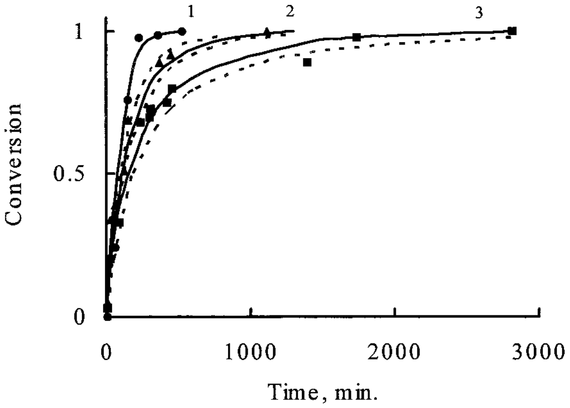
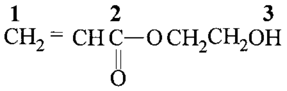


Fig. 4. Kinetics of model reaction of ethylacetate with sodium etoxide in ethanol solution at 25°C (solid lines). Designation of kinetic curves and initial concentration of components are given in Table 3. Calculated kinetic curves are designated by dotted lines.

Conclusion

The monomers studied under the conditions of anionic polymerization display activity towards initiating and propagating anions simultaneously in three points as indicated in the scheme:



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

Such plural reactivity defines the polymerization mechanism, summarized in the following simplified kinetic scheme:

Initiation $$I + M \xrightarrow{k_i} R_1O^-$$

Chain propagation $$R_1O^- + M \xrightarrow{k_p} R_2O^-$$

$$\cdots\cdots\cdots\cdots$$

$$R_jO^- + M \xrightarrow{k_p} R_{j+1}O^-$$

$$R_jO^- + R_iOH \xrightarrow{k_p} R_{j+i}OH$$

$$j = 1, 2, 3 \,....., \qquad i = 1, 2, 3 \,.....$$

Proton transfer

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

$$k_{tr1} >> k_p \; ; \quad K_1 = \frac{k_{tr1}}{k_{tr2}} \sim 1$$

Chain transfer on polymer

$$R_jO^- + R_i\,OH \overset{k_a}{\rightleftharpoons} (\mathrm{Adduct})^- \overset{k_{tr}}{\rightleftharpoons} R_iOCH_2CH_2COOR_{j\text{-}k} + {}^-OCH_2CH_2OR_{k\text{-}1}OH$$

$$k_a >> k_p; \quad K_a >> 1$$

Chain termination

$$R_j\,O^- + H_2O \rightleftharpoons R_j\,OH + HO^-$$

$$HO^- + R_j\,OH \xrightarrow{k_t} R_{j\text{-}k}OCH_2CH_2COO^- + HOCH_2CH_2OR_{k\text{-}1}OH$$

Initiated by alkali metal polymerization, cyclization and chain transfer reactions of t-butoxide anion on polymer with alkyl-oxygen scission discussed ahead are not taken into account in this scheme.

The polymerization mechanism due to the heterogeneous development combines features of chain growth and step growth polymerization.

Acknowledgements

Author is grateful to the Russian Foundation for Basic Research (Project 01–03– 97007) and International Science and Technology Center (Project 02-1918) for the financial support.

[1] A.S. Matlack, Pat. 2672480 USA (1954).
[2] D.S. Breslow, G.E. Hulse, A.S. Matlack, J. Am. Chem. Soc., **1957**, *79*, 3760.
[3] M. Guaita, G. Camino, L. Trossarelli, Makromol. Chem., **1970**, *131*, 309.
[4] T. Saegusa, S. Kobayashi, Y. Kimura, Macromolecules, **1974**, *7*, 256.
[5] T. Saegusa, S. Kobayashi, Y. Kimura, Macromolecules, **1975**, *8*, 950.
[6] Y. Yamada, T. Matsushita, T. Otsu, J. Polym. Sci., Polym. Lett. Ed., **1976**, *14*, 277.
[7] S. Kobayashi, J. Kadokawa, I.-F. Yen, H. Uyama, S. Shoda, Macromolecules, **1992**, *2,5* 6690.
[8] T. Iwamura, I. Tomita, M. Suzuki, T. Endo, J. Polym. Sci., Polym. Chem., **1998**, *36*, 1491.
[9] T. Iwamura, I. Tomita, M. Suzuki, T. Endo, Reactive and Functional Polymers, **1999**, *40*, 115.
[10] J. Kadokawa, Y. Kaneko, S. Yamada, K. Ikuma, H. Tagaya, K. Chiba, Macromol. Rapid Commun., **2000**, *21*, 362.

[11] B.A. Rozenberg, B.A. Komarov, G.N. Boyko, E.A. Dzhavadyan, A.I. Perekhrest, G.A. Estrina, Polym. Sci., **2001**, ***43A.,*** 799.
[12] B.A. Rozenberg, L.M. Bogdanova, E.A. Dzhavadyan, B.A. Komarov, G.N. Boyko, L.L. Gur'eva, G.A. Estrina, Polym. Sci., **2003**, ***45A.,*** ???????.
[13] B.A. Rozenberg, G.A. Estrina, Ya.I. Estrin, Polym. Sci., submitted.
[14] B.A. Rozenberg, G.N. Boyko, L.M. Bogdanova, E.A. Dzhavadyan, B.A. Komarov, P.P. Kusch, G.A. Estrina, Polym. Sci., in press.
[15] B.A. Rozenberg, G.N. Boyko, L.L. Gur'eva, E.A. Dzhavadyan, B.A. Estrina, Polym. Sci., in press.
[16] M. Iijima, Y. Nagasaki, M. Kato, K. Kataoka, Polymer, **1997**, ***38,*** 1197.
[17] C.Zune, R.Jerome, Prog. Polym. Sci., **1999,** *24,* 631.
[18] B.A. Rozenberg, V.I. Irzhak, N.S. Enikolopov, Interchain exchange of polymers, Chemistry, Moscow: **1975**.