Macromol. Symp. **2005**, *227*, 373-382

Features of the Morphology of 2-Hydroxyethyl Acrylate ω-Polymer

Boris Rozenberg,[1] *Anatolii Chalykh*[2]

[1]Institute of Problems of Chemical Physics, Russian Academy of Sciences, acad. Semenov avenue 1, 142432 Chernogolovka Moscow region, Russia
Fax: (+7) 096 5227763; E-mail: rozen@icp.ac.ru
[2] Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii prospect 31, Moscow 117915, Russia

Summary: Ω-Polymer of 2-Hydroxyethyl acrylate (HEA) with nanoporous morphology is formed and characterized. Some kinetic peculiarities and mechanism of HEA low-temperature ω-polymerization is discussed. It is suggested to use ω-polymerization of vinyl monomers for preparation of functionalized nanoporous polymer composites for different .technical and biomedical applications.

Keywords: 2-hydroxyethyl acrylate; nanoporous polymer composites; ω-polymerization

Introduction

One of the specific types of nanocomposites is nanoporous composites where air or other gas serves as specific filler. Some ways of preparation of nanoporous composites have been elaborated.[1, 2]

The purpose of the paper is to demonstrate that the process of ω-polymerization that chemists always considered as a very harmful side reaction in polymer technology can be used for production of useful nanostructured porous products.

The free-radical polymerization of numerous vinyl and divinyl monomers or their mixtures in bulk or solution initiated using material initiators, photo chemically, thermally, or by any other method, can pass to the regime where micro heterogeneous nuclei appearing by chance in the initial homogeneous system continue to develop in the auto acceleration mode.[3–7] Eventually, a highly porous, nontransparent, cross linked polymer insoluble in organic media is formed. A seed of ω-polymer, once placed in a fresh portion of the monomer, induces ω-polymerization not only of its own monomer but also of any other monomer capable of free-

DOI: 10.1002/masy.200550938

radical polymerization and even monomers whose polymerization is never accompanied by transition to the polymerization mode.

Pravednikov and Medvedev[8,9] formulated the principal features of the mechanism of ω-polymerization. They first advanced an idea concerning the decisive role of gel-like microheterogeneous particles arising from the radical polymerization of vinyl monomers. These particles appear due to the occurrence of a chain transfer to the monomer or polymer with subsequent recombination of macro radicals or the existence ω of cross linking agents bearing two or greater number of double bonds in the reaction system. Because of the local increase in the viscosity of the microgel, the rate of termination of growing chains drops sharply and the local concentration of free radicals increases. Naturally, this causes acceleration of polymerization of the monomer diffusing from the bulk inside the micro gel.

The accumulation of the monomer in the micro gel volume brings about the growth of osmotic pressure and, eventually, when a certain osmotic pressure is achieved, leads to the mechanical rupture of network chains and the generation of two new free radicals in each chain rupture event. This scenario of ω-polymerization was convincingly proved by experiments on polymerization induced by ^{14}C-labeled nucleus ω-polymer[8,9] and by detection of the photo elastic effect.[10] Moreover, the ESR study of the ω-polymerization of butyl methacrylate initiated by the ω-polymer seed provided straightforward evidence in support of the mechanochemical formation of free radicals.[5] The feasibility of this initiation in ω-polymerization was demonstrated by elegant experiments on the initiation upon addition of the as freshly notched glassy polymer in the reaction mixture. [11]

It is obvious, that the mechanism of ω-polymerization advanced in[8,9] was substantiated by numerous experimental data and is currently considered to be generally accepted.

Thus, we can define ω-polymerization as such a type of chain radical polymerization of vinyl monomers proceeding micro heterogeneously in the gel-phase in the auto accelerated mode due to the mechanochemical rupture of stressed crosslinked chains caused by osmotic pressure of the monomer diffusing from the parent phase into the gel-phase. Transformation of the conventional radical polymerization into the ω-polymerization mode is caused when polymerization in microgel particles appear in the polymerization system by either reason (on account of chain transfer on a monomer or polymer, presence of crosslinking agents, etc.) accelerates due to the topologically hindered chain termination.

The focus of this paper is to gain a deeper understanding of the features of the morphology of forming the ω-polymer and its relation to the ω-polymerization mechanism.

Experimental

We used HEA (Air Products and Chemicals Inc.) with T_b= 90–92°C/1600 Pa. The nitroxyl radical, 2,2,6,6-tetramethyl-1-piperinyloxy (TEMPO), with T_m= 33°C was used as received. The reaction kinetics was studied at 30°C by isothermal calorimetry using a DAK-1-1 thermal analyzer. The enthalpy of HEA polymerization was taken equal to –75 $kJ\cdot mol^{-1}$. Kinetic measurements were performed using sealed ampoules containing weighed portions of the tested substance from which dissolved air was preliminarily removed. Complete removal of oxygen from the reaction system was achieved by repeating many times freezing of the ampoule with the reaction system in liquid nitrogen, its evacuation, and thawing.

Visual changes of the reaction system in the course of ω-polymerization were recorded on a video camera connected to a microscope and were written down as a digital file. The consumption of TEMPO was monitored with an ESR-21 radiospectrometer at 77 K.

The glass transition temperature of ω-polymers was measured by DSC (Mettler-Toledo DSC 822e thermal analyzer).

Morphological characteristics of ω-polymers were determined by transmission and scanning electron microscopy (TEM and SEM). Samples for TEM were prepared by breaking of piece of ω-polymer by vibrodisperser in liquid nitrogen. Particles from 50 to 500 nm were deposited on a carbon substrate and studied on electron microscope EM-301 with a high-resolution table at voltage amplification from 60 to 100 KeV. Direct magnification is changed from 10,000 to 100,000 times.

Samples of ω-polymer for SEM were prepared by Au sputtering in a vacuum with thickness more than 200 nm. Samples were studied on scanning electron microscopes JSM-U3 (Jeol) and SEM-500 (Phillips). Particle size distribution and pore size distribution were measured by treatment of micrographs by standard procedure.

The specific surface of the ω-polymer was measured using gasometric technique by low–temperature adsorption of nitrogen. Samples of ω-polymer (~0.5 g) were maintained for 2 h in a nitrogen stream at 120°C. The instrument was preliminarily calibrated using samples with a known specific surface.

Kinetic features of HEA ω-polymerization

The polymerization of interest can be arbitrarily divided into 3 stages: ripening during which metastable microgel particles appear, formation of separate stable nuclei localized in the bulk as nontransparent white inclusions, and rapid polymerization of the monomer, accompanied by a significant increase in the reaction volume. No signs of polymerization are observed at the ripening stage. The appearance of stable nuclei capable of further growth can be detected both visually and calorimetrically. These stages of ω-polymerization are well observable and may easily be recorded on a video camera connected to the microscope. Several photographs taken at various moments of the polymerization experiment are presented in Figure 1. Unlike the linear poly(2-hydroxyethyl acrylate) (PHEA) prepared through radical polymerization, the polymer under examination is insoluble in water, ethanol, chloroform, and other organic solvents, including DMF, which convincingly demonstrates formation of the cross linked polymer. The glass transition temperature of the ω-polymer, estimated by DSC was found to be –5°C, whereas the glass transition temperature of the linear PHEA prepared via the radical polymerization of HEA induced by benzoyl peroxide is –16°C.

The most clearly pronounced kinetic feature of ω-polymerization is its auto-accelerated character.[6,7] Nevertheless, we failed to detect growing radicals directly using ESR spectroscopy, (the instrument sensitivity was $<10^{14}$ spins/g).[7] However, the presence of the growing radicals and all their kinetic characteristics can be determined easily using the ESR technique by consumption kinetics of the added stable nitroxyl radical TEMPO. Addition of the seed of the ω-PHEA for a long time exposed on air to HEA leads to the rapid development of HEA polymerization upon ω-polymer swelling in the monomer (Fig. 2, curve 1). This result suggests that observed HEA ω-polymerization in auto-accelerated mode was initiated by free radicals that appeared due to the rupture of the swelled seed.

It was found quite unexpectedly the ω-polymerization proceeds even in the presence of the nitroxyl radical, which is usually a strong inhibitor for free-radical polymerization (Fig. 2). However, in this case, TEMPO behaves as a weak inhibitor (decelerator) rather than a strong one.[7] Another interesting feature of HEA ω-polymerization is the observed dependence of the induction period on the weight of the reaction system. The rate of generation of free radicals in the spontaneous ω- polymerization of HEA estimated from the kinetics of consumption of nitroxyl radicals using ESR spectroscopy[7] is equal to $w_i = 1.7\times10^{-8}\ \mathrm{mol\cdot l^{-1}\cdot s^{-1}}$.

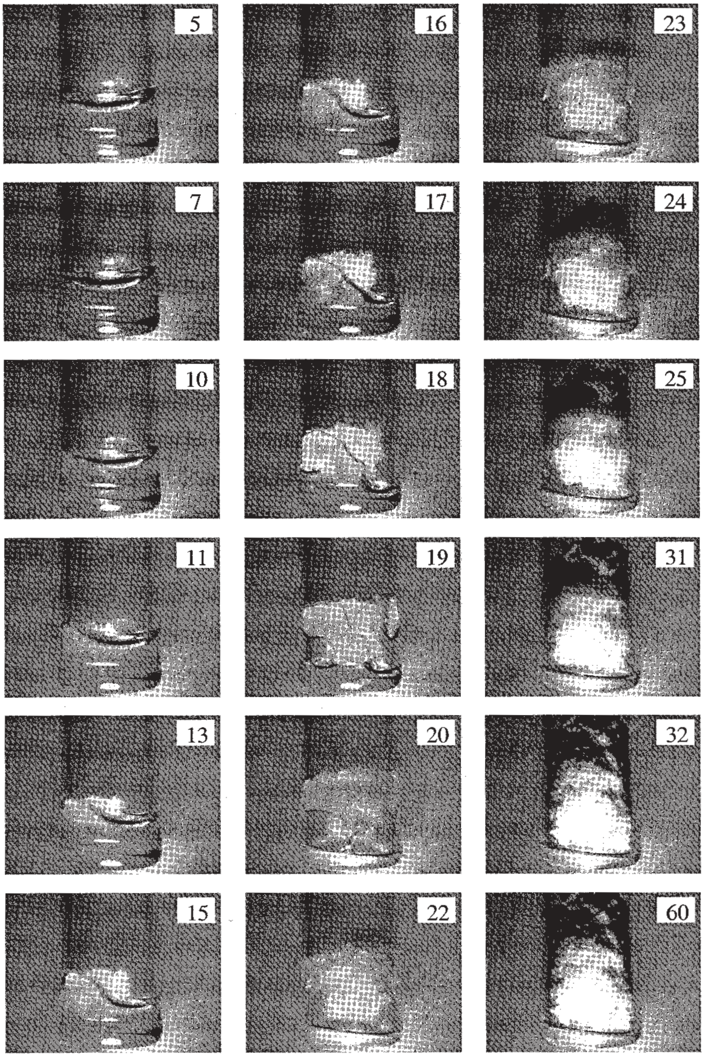

Figure 1. Kinetics of-polymerization of HEA at room temperature. Numbers on figures denote time in minutes from the appearance of the first nuclei in the reaction system.

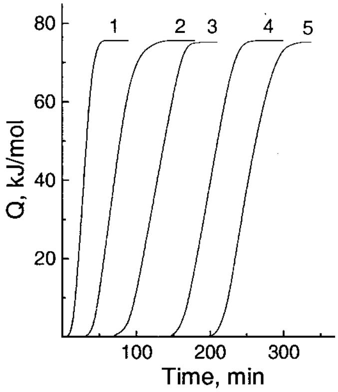

Figure 2. The kinetic curves of HEA ω-polymerization at 30°C upon seeding of ω-polymer (1), in the absence of seed additive (2), and in the presence of TEMPO additives, mol·l^{-1}: 1×10^{-5} (3), 1×10^{-4} (4), and 1×10^{-3} (5). The conversion of HEA in all cases is complete. Q_∞=75kJ·mol^{-1}.

Initiation mechanism

Usually, a certain initiation source is present in ω-polymerization. However, in the case under consideration, it is absent and the reaction proceeds spontaneously at rather low temperatures, when the thermal initiation is impossible. An essentially important question arises: what mechanism is responsible for generation of primary free radicals at low temperatures? The absence of radiation background in our laboratory gives us reason to discard the radiation initiation hypothesis. The photo initiation hypothesis should also be ruled out, because the monomer freed from traces of oxygen by purging with argon remains stable upon prolonged exposure to light at room temperature. The finding that the greater the number of freeze–pump–thaw cycles in the course of monomer degassing, the shorter the induction period in HEA polymerization, leads us to hypothesize about the mechanochemical origin of primary free radicals that result from temperature jumps in the glassy monomer during its freezing and thawing.[7]

Morphology

Formation of the highly porous nontransparent polymer is the most characteristic, visual feature of ω-polymerization. Figure 3 shows the micrographs obtained by TEM and SEM techniques. These micrographs distinctly show that ω-polymer has a nanoporous fractal-type

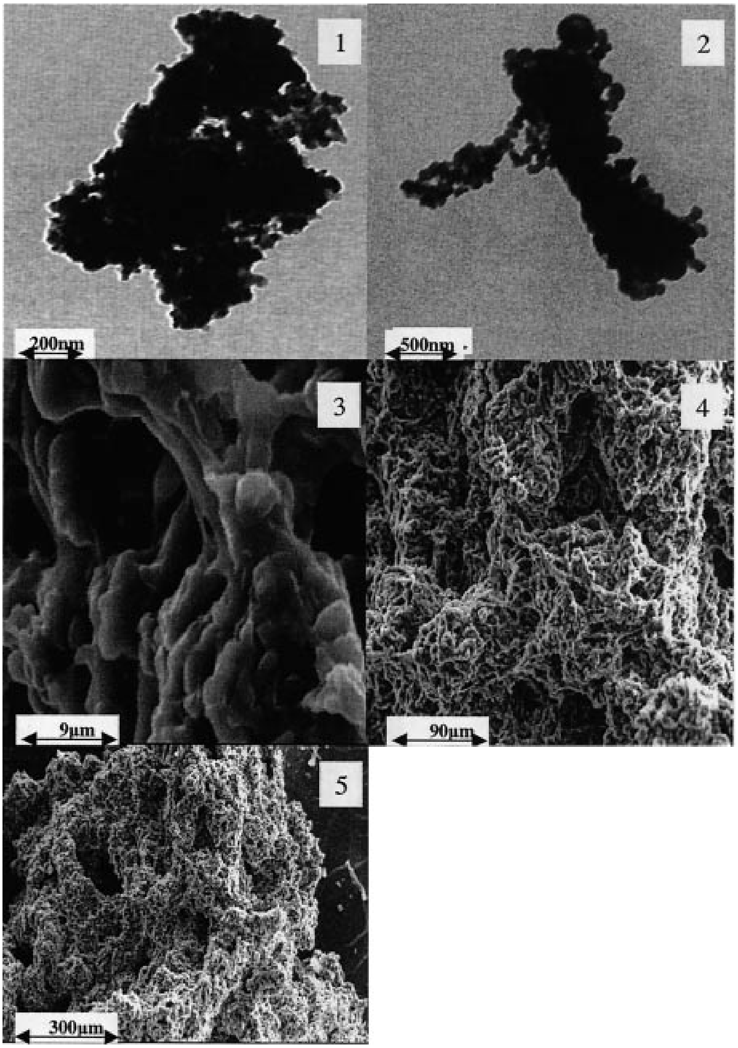

Figure 3. TEM 1-2 and SEM 3-5) micrographs.

structure with communicating interstices. All investigated particles represent nanoporous conglomerates of nanoparticles from 10 to 200 nm (Fig. 4). About 60% constitute particles with an average size equal to 60 nm. The pronounced similarity of the pore size distribution on different scales (Figs. 5 and 6) is observed. The measured value of the specific surface (1.3 $m^2 \cdot g^{-1}$) is consistent quantitatively with the TEM and SEM data discussed above.

Let us consider the possible ways of formation of ω-polymer with the obtained unique morphology. The evolution of highly volatile compounds in the course of polymerization could be considered as an evident reason for the formation of the porous polymer. However, this supposition is inconsistent with the observed kinetic and structural data discussed in details in[6]. It is obvious, that the highly porous structure of ω-polymers is tightly associated with the mechanism of ω-polymerization. It related to the formation of new interfaces upon the mechanochemical breakdown of growing polymer particles because of internal stresses developing in the formed polymer. This effect plays a decisive role in the sharp increase in the volume of the polymerizing system and in the auto acceleration of ω-polymerization. Formation of new interfaces not only increases the number of free radicals in the system but also makes macro radicals accessible to monomer molecules that are located inside and outside the growing particle and in the initial continuous parent phase. In other words, the breakdown of particles arising in ω-polymerization represents a peculiar mechanism of component mixing in the heterophase polymer system. The considered mechanism of ω-polymerization must result in a nanostructured ω-polymer. It is interesting to note, that beside pores of nano size, micron size pores exist as well. The most probable reason for the appearance of these micron-size pores is diffusion of the monomer inside the growing micro gel particles. The final morphology of the ω-polymer is determined by competition of the monomer diffusion rate inside the growing micro gel from the parent phase, and the integral rate of initiation and "mixing mechanism" which determine the rate at which growing radicals are delivered into the parent phase.

Conclusion

A new mechanism of ω-polymerization of vinyl monomers proceeding at room and lower temperatures was first studied in this work using HEA polymerization as an example. Primary

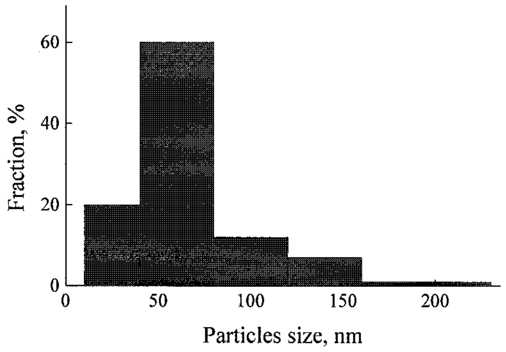

Figure 4. Distribution of particles on sizes.

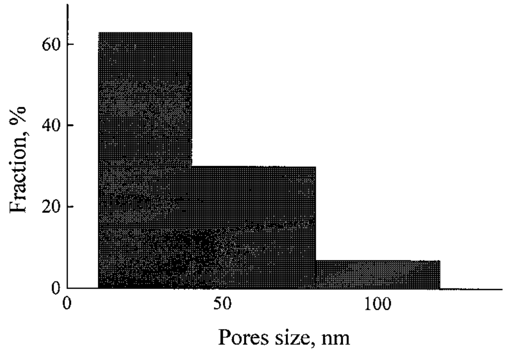

Figure 5. Distribution of pores on sizes by TEM data.

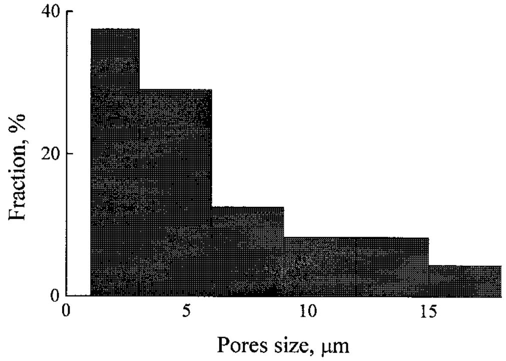

Figure 6. Distribution of pores on sizes by SEM data.

free radicals initiating this process are generated mechanochemically through multiple freeze–pump–thaw cycles upon vacuum degassing of the monomer. TEM and SEM morphological studies are revealed that generated ω-polymer has unique nanoporous fractal type structure with communicating interstices. Such type of ω-polymers bearing functional group in every unit of the chain can be perspective for utilization them as carriers for preparation of effective heterogeneous catalysts, sorbents and for many other technical and biomedical applications. Some recent patent publications[12] referring to ω-N-polyvinylpirrolidone confirm this supposition.

Acknowledgement

Authors are grateful to the Russian Foundation for Basic Research (Project 01–03–97007 and 04-03-32674), Division of Chemistry and Materials Sciences Russian Academy of Sciences (Project 04-12-131) and International Science and Technology Center (Project 02-1918) for the financial support.

[1] A.L. Volynskii, N.F. Bakeev, "*Highly Dispersed Oriented State of Polymers*", (in Russian), Chemistry, Moscow **1984**.
[2] M.P. Tsurupa, "*Supercrosslinked polystyrene*", doctor degree dissertation, (in Russian) Moscow: INEOS RAS, **1984**.
[3] Kh.S. Bagdasaryan, "*The Theory of Free-Radical Polymerization*", (in Russian), Akad. Nauk SSSR, Moscow **1959**, p. 173.
[4] J.W. Breitenbach, *Adv. Macromol. Chem.*, **1968**, *1*, 139.
[5] V.A. Kabanov, M.B. Lachinov, E.E. Makhaeva, S.G. Starodubtsev, V.B. Golubev, *Chem. Phys., (in Russian)*, **1991**, *10*, No. 11, 1512.
[6] B.A. Rozenberg, E.A. Dzhavadyan, *Polym. Sci., Ser. A*, **2003**, *45*, No. 12, 1174.
[7] B.A. Rozenberg, E.A. Dzhavadyan, S.I. Kuzina, A.I. Mikhailov, *Polym. Sci., Ser. A*, **2003**, *45*, No. 12, 1167.
[8] A.N. Pravednikov, S.S. Medvedev, *Dokl. Akad. Nauk SSSR*, **1955**, *103*, No 3, 461.
[9] A.N. Pravednikov, S.S. Medvedev, *Dokl. Akad. Nauk SSSR*, **1956**, *109*, No. 4, 579.
[10] J.W. Breitenbach, H. Dworak, *J. Polym. Sci.*, **1966**, *4*, 1328.
[11] J.W. Breitenbach, H. Burgmann, *Makromol. Chem.*, **1966**, *90*, 298.
[12] United States Patent 6,677,417 (2004), BASF Aktiengesellschaft, invs.: H. Meffert et al.: web-site.