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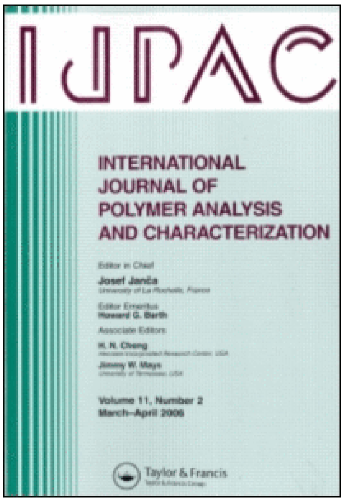

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Reactions of Functional End Group Redistribution over Macromolecules and their Characterization by Liquid Chromatography Under Critical Conditions

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Reactions of Functional End Group Redistribution over Macromolecules and their Characterization by Liquid Chromatography Under Critical Conditions

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Anionic polymerization of 2-hydroxyethylacrylate (HEA) and 2-hydroxyethylmethacrylate (HEMA) proceeding with formation of heterochain ether-ester oligomers was studied. Functionality type distribution of oligomers was characterized by liquid chromatography under conditions close to critical ones. Presence of macromolecules having different kinds of end groups (two acrylate, one acrylate and one hydroxyl, two hydroxyl groups on a molecule), as well presence of cyclic molecules was shown in oligomers. This fact indicates existence of intensive interchain exchange reactions in the course of polymerization. The possibility of carbon chain fragment formation was shown also. The mechanism of side reactions resulting in redistribution of functional end groups over macromolecules is revealed.

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INTRODUCTION

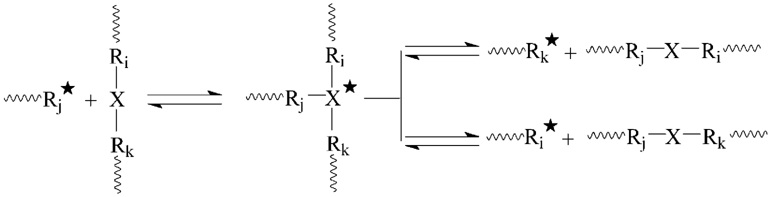
Many processes of polymer synthesis are accompanied by interchain exchange reactions proceeding with the rupture of the main chain and resulting in redistribution of the functional groups between macromolecules. Such reactions are typical for the formation of various heterochain polymers (polyesters, polyamides, polyethers, polyacetals, polysulfides, polysiloxanes, phosphorus- and metal-containing polymers, etc.) generated by polycondensation and/or ionic or radical chain polymerization[1–3]. A general simplified scheme of such reactions is shown in Scheme 1.

When the active propagating center attacks its own macromolecule, a macrocycle is formed due to the intramolecular chain exchange reaction, shown in Scheme 2.

It is obvious that both reactions lead to the redistribution of macromolecules over the length and type of end functional groups[1].

Interchain exchange reactions are a rather useful mechanism for preparation of block and random copolymers, polymer blends from incompatible polymers, introducing functional end groups into macromolecules, etc.[1–4]. At the same time, these reactions prevent the synthesis of polymers with necessary characteristics, namely structure of the backbone, molecular weight distribution (MWD), and distribution of end functional groups over macromolecules. The latter is especially important for preparation of oligomers with definite end group functionality.

Identification of chain exchange reaction proceeding during polymer formation is also rather difficult because these reactions do not practically change average characteristics of polymers such as molecular weight (MW), type of backbone, and concentration and nature of end functional groups. That is why the majority of conventional techniques for polymer characterization (infrared, ultraviolet, and nuclear magnetic resonance (NMR) spectroscopy, chemical analysis, etc.) do not allow chain exchange reactions to be identified even qualitatively. At the same time,



SCHEME 1 X is O, N, S, Si, P, etc., and ∿∿$R_j^{\star}$ is the active propagating macromolecule (cation, anion or radical).

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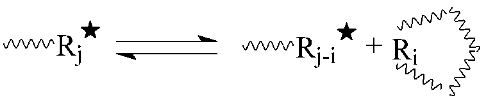


SCHEME 2 Formation of macrocycle.

data on a real composition of macromolecules, i.e., on the functionality type distribution (FTD) of the reacting system, are extremely important not only from an academic point of view, but also from a 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.

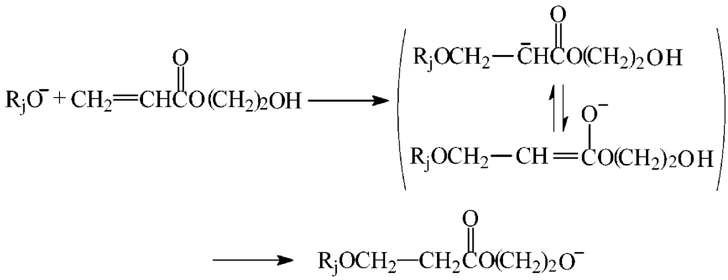
In particular, such a problem arose while studying anionic polymerization of (meth)acrylates containing a mobile hydrogen atom [5–9]. This reaction occurs via proton transfer in each propagation act and yields polyesters that cannot be otherwise obtained. Scheme 3 shows the mechanism of such polymerization for 2-hydroxyethylacrylate (HEA).

The resulting polymer has the acrylate double bond on one end of the molecule and the hydroxyl group on the other end, i.e., it is a macromonomer. However, the chain propagation is accompanied by side reactions, mainly by interchain exchange proceeding via transesterification mechanism[5–8].

This reaction yields, in addition to the target product (macromonomer), macromolecules containing the acrylate groups on both ends (polyesterdiacrylates) and an equivalent amount of macromolecules with two hydroxyl end groups (polyesterdiols).

As it is shown from Scheme 4, the average composition of the oligomer as well as the general content of the functional end groups do not change in the course of the interchain transesterification reaction.

It is worth noting, that the intrachain transesterification reaction through attack of propagating species on ester group results in linear chains only [6–8].



SCHEME 3 HEA polymerization.

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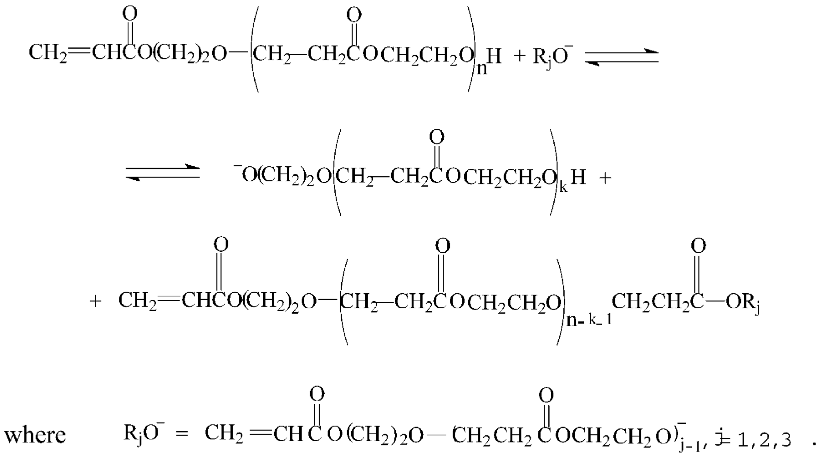

SCHEME 4 Side reactions of HEA polymerization.

Undoubtedly, in order to develop methods to suppress these side reactions and, hence, to obtain products of desired structure, adequate analytical techniques for quantitative estimation of the intensity of the side reactions should be worked out.

Liquid chromatography under conditions close to critical one (the regimes being intermediate of adsorption and exclusion ones) is one of the most efficient methods for analysis of FTD of macromolecules. Under the 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 excluded volume, and retention volumes of functional macromolecules are mainly determined by the nature and number of functional groups[10,11]. Retention volumes of cyclic macromolecules are usually bigger than those of linear bifunctional ones, while for branched macromolecules they are smaller than those of linear ones of the same functionality.

In this article, the methods for chromatographic analysis of FTD of oligohydroxyethyl(meth)acrylates (OHEA and OHEMA) are presented, and application of the results for determining the nature and intensity of side reactions during oligomers synthesis is shown.

RESULTS AND DISCUSSION

The FTD concept was formulated by Entelis et al. 1971[12,13], at the same time adsorption column chromatography was used for separation of

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hydroxyl terminated oligoethers over functionality type of macromolecules[14]. Belen'kii et al.[15] demonstrated separation of polyols containing up to five hydroxyl groups per molecule by the thin-layer chromatography (TLC) method. The critical character of the adsoption-exclusion transition predicted by DiMarzio and Rubin[16,17], was demonstrated by Belen'kii et al. using TLC method for polystyrene samples[18].

During the past two decades, the quantitative theory of liquid chromatography under critical conditions has been developed by Entelis et al.[10,11], and Gorbunov and Skvortsov[19].

Most important for practical goals is the procedure of pre-calculation of the eluent composition providing the conditions of elution close to the critical ones especially for functional oligomer analysis[10,11]. The procedure uses the parameter of Snyder's quantitative correlation theory of adsorption and liquid chromatography of low-molecular compounds[20]. The group increments suitable for individual compounds are used for calculating the value of adsorption energy of the repeated units of polymer or oligomer.

FTD analysis of functional oligomers, in particular, oligoester diols[21,22], epoxy resins[23], hydroxyoligobutadienes[24,25], etc., has been performed under the critical conditions.

Berek[26] and then Maco and Hunkeler[27] recently published extensive reviews dealing with critical chromatography of various polymers, copolymers, and oligomers, including FTD analysis of functional oligomers.

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Selection of Critical Conditions

Two ways to select critical conditions have been used. For the first method, a set of well-characterized functional-free and monofunctional samples of polymers with narrow MWD and known values of MW in the wide range is necessary. After pre-calculation of the composition for binary eluent, which provides critical conditions for the particular polymer (according to Dimarzio and Rubin[17], and Belen'kii et al.[18]), the dependence of the retention volume of functional-free polymers on their MW is determined. If retention volumes grow with MW increase (adsorption mode), the eluent composition is changed to increase the concentration of a stronger component. If retention volumes reduce with MW growth (exclusion mode), the concentration of a weaker component is increased. After several iteration steps, the eluent composition is selected, which provides independence of retention volume on MW. To refine the eluent composition, monofunctional samples are used because dependence of retention volume on MW increases essentially if a strongly adsorbed functional group is available in the macromolecule. Varying of the column temperature provides more exact definition of elution conditions.

This method for selection of critical conditions is the most reliable. In particular, it was used for the development of the method of FTD analysis of hydroxypolybutadienes[25]. It has been shown that for both functional-free and monofunctional macromolecules, retention volumes do not depend on MW in the MW range of 2500 to 70000. However, this method cannot be used for many types of polymers because there are no appropriate sets of samples with well-defined MW and functionality. In this case the second method is used, which involves samples with a wide MWD and unknown FTD. After pre-calculation of the binary eluent composition, the chromatogram for this composition is analyzed. For the adsorption mode, two or three groups of peaks with partial overlapping are available. For the exclusion mode, there are many fewer peaks, and they are broadened and partially overlap. After several correction steps, such composition of the eluent can be chosen, which provides the minimum number of the narrowest peaks, with the first of them being near the excluded volume. Under the critical conditions chromatograms have almost identical views for the samples having different MW, i.e., peaks of the same functionality type have similar retention volumes.

As far as the average functionality of the sample is known, the calculation of the average functionality from chromatograms can be additional evidence of separation over functionality only.

At oligomer synthesis of HEA and 2-hydroxyethylmethacrylate (HEMA), we could only vary average values of oligomer MW with rather wide MWD (polydispersity coefficient ~2). Methods for synthesis of such oligomers with narrow MWD and known functionality are not available now. Therefore, critical conditions were determined using the second way.

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Liquid Chromatography of OHEA Under Critical Conditions

Pre-calculations of critical conditions for the polymer with a repeated unit of the backbone being (–$CH_2CH_2COOCH_2CH_2O$–) were performed using the scheme and numerical parameters from Entelis et al.[13]. The power of the eluent for elution of such polymer under critical conditions appeared to be ~0.4 (with silica gel as the sorbent). This value is close to the elutriating force of methyl ethyl Ketone (MEK) ($\varepsilon = 0.393$), which is also a good solvent for OHEA.

As Figure 1 shows, if neat MEK is used for elution, the chromatogram has adsorption character (chromatogram 1). Thus, to transform to critical conditions, a stronger eluent should be added. So, 1,4-dioxane (DO, $\varepsilon = 0.43$) and methanol ($\varepsilon = 0.73$) were used as the second component.

In Figure 1, the chromatograms are presented, that were obtained for different MEK:DO ratios at ambient temperature (chromatograms 2, 3) and at the column temperature 60°C (chromatogram 4). It can be seen

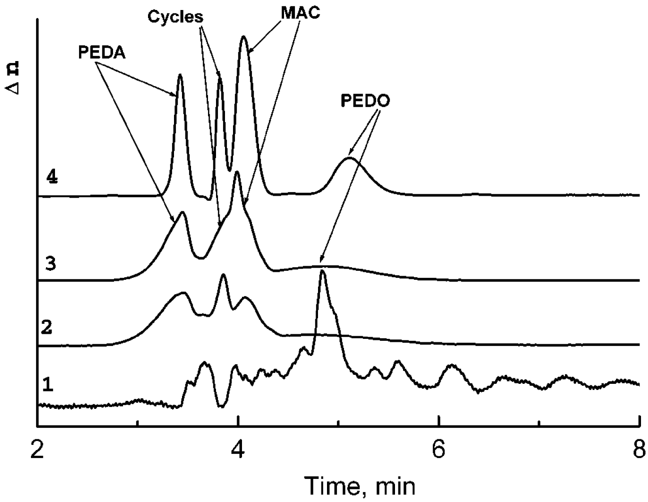

FIGURE 1 Chromatograms of OHEA ($\bar{M}_n = 1400$); 1, eluent MEK at 25°C; 2, MEK/DO (75/25) at 25°C; 3, MEK/DO (85/15) at 25°C; 4, MEK/DO (85/15) at 60°C. Detector: refractometer.

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that the latter can be considered a classical example of chromatography near the critical point. The first peak (polyesterdiacrylates, PEDA) corresponds to macromolecules without strongly adsorbed hydroxyl groups. The second peak can be identified as a fraction of cyclic macromolecules (macrocycles, MC). The third peak corresponds to macromolecules with one end hydroxyl and one vinyl group (macromonomer, MAC), and the last broad peak corresponds to macromolecules bifunctional over the hydroxyl group (polyesterdiols, PEDO). Peak assignment by polarity of components was confirmed also by several other methods.

After OHEA had been treated with acryloylchloride and all hydroxyl groups had been converted to acrylate ones, two peaks only were left in the chromatogram, an intense peak with retention time about 3.4 minutes, and a small peak with retention time ~4.1 minutes, those peaks corresponding to PEDA and fraction of cyclic products. Figure 2 shows the chromatogram of the exhaustively acrylated OHEA. Two expected fractions were separated quite satisfactorily.

Useful information about the second fraction structure could be obtained by its mass-spectroscopic analysis after its preparative isolation. However, preparative separation of fractions by using a refractometric detector appeared to be impossible because of a strong broadening of the peaks after its outlet from the measuring cell related to the features of refractometer design. To solve this task, we tried to use a spectrophotometric detector

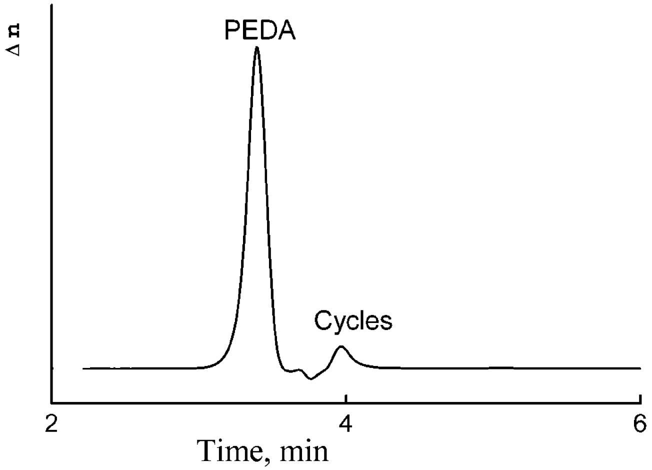

FIGURE 2 FTD chromatogram of exhaustively acrylated OHEA ($\bar{M}_n = 2400$). Eluent is MEK/DO (85/15), 0.7 mL/min, column temperature 60 °C, refractometric detector.

that is not characterized by such broadening. The ester group is known to absorb weakly in 210–215 nm range, while the acrylate group containing the C = C bond absorbs intensely in this range. However, MEK is considered to be transparent beginning from 300 nm and, hence, seems to be unsuitable for detecting HEA oligomer fractions. Hovewer, we disclosed a transparent window for MEK in the region of 210–220 nm. Meanwhile, although DO is quite transparent in this region, its mixture with MEK appeared to be almost nontransparent. Therefore we selected the critical conditions for OHEA using a MEK/methanol mixture, which is transparent enough in the region of 210–220 nm. A very unusual fact was observed in this case: although retention volumes of the linear fractions of oligomer remained almost without change in comparison with the MEK/DO mixture, retention volume of the cyclic fraction increased and became larger than the retention volume of the monofunctional fraction at MEK/methanol mixture under the critical conditions. We have not found any satisfactory explanation of this experimental fact so far. A hypothetical cyclic fraction was isolated using a MEK/methanol mixture as the eluent, and exhaustively acrylated OHEA was used as a sample.

In this case, there was no overlapping of the fractions. For accumulation of the fractions, the increased injection loop was used (50 μl instead of 20 μl for analytical separations) and higher solution concentration (~ 50 mg/mL). About 50 mg of oligomer was separated in 20 runs.

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For the hypothetical cyclic fraction, the mass spectrum was obtained by mass spectroscopy with electro spray ionization technique (ESI MS) providing the spectrum of molecular ions without molecule fragmentation. As follows from the mass spectrum (Figure 3), ions with m/z = 225 and 233 are the major components, and they can be identified as $(C_5H_8O_3)_2Na^+$ and $(C_5H_8O_3)_2H^+$, respectively. In addition, much less intense peaks of ions with m/z = 371 and 349 are available. These masses correspond to ions $(C_5H_8O_3)_3Na^+$ and $(C_5H_8O_3)_3H^+$. The peak with m/z = 487 can correspond to tetramer $(C_5H_8O_3)_4Na^+$. There are no ions with the masses corresponding to the monomer. It can be stated that cyclic molecules in oligomers are mainly presented by dimer cycles, with a small content of trimer cycles and, possibly, of tetramer cycles.

The following arguments prove the peak assignment made above:

1. The sequence of the peak output corresponds to the critical chromatography theory;
2. The values of volume retention of the first peak in Figure 1 is identical to the value for the main peak of the exhaustively acrylated OHEA (Figure 2) and corresponds to the value of exclusion volume of the column;
3. The relative integral intensity of the main peaks for PEDA, MAC, and PEDO (trace 4 on Figure 1) is near to the 1:2:1 relation. Such relation

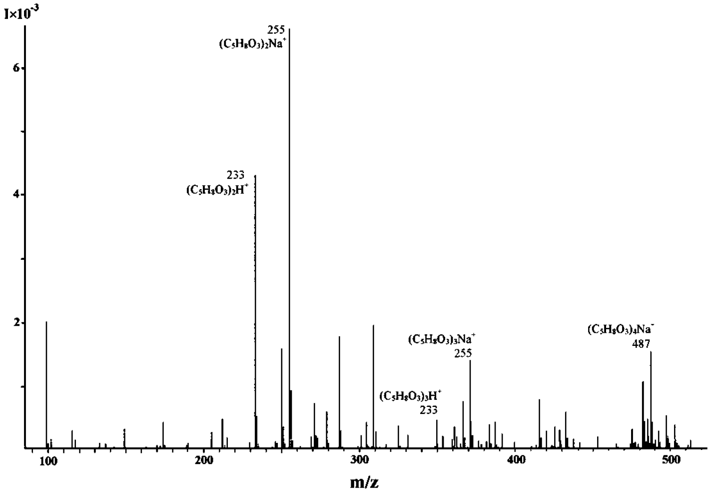

FIGURE 3 ESI mass spectrum of the cyclic fraction of OHEA. The mass spectrum was measured by V. I. Kozlovskii at the Branch of the Institute of Energetic Problems of Chemical Physics in Chernogolovka, Russian Academy of Sciences.

corresponds to the statistical relation of quantities of diacrylate: monoacrylate-monool:diol, which must be formed as a result of the interchain exchange reactions;

4. The intensities of the PEDA and MAC peaks are almost equal on the UV trace at 215 nm (see Figure 4), but the intensities of both the PEO and the cyclic peaks are very small. It signifies that content of the acrylates groups in the PEDA fraction is twice that in the MAC fraction, but the PEO and cyclic fractions do not contain any acrylate groups. (The extinction coefficient of the acrylate groups at 215 nm is much larger than the extinction coefficient of saturated ester groups.)

Unfortunately, quantitative determination of the end group content by integral intensity of the UV trace of the peaks is impossible in this case – although eluent transparency at 210–220 nm is sufficient for peak detection, it is not enough for quantitative measurements.

So, the results of oligomer FTD show not only the interchain exchange side reactions, but also the cycle formation during anionic polymerization of HEA. Cyclic products in the considered case can be formed at attack of propagating alkoxy anion on double bond of its own macromolecule; see Scheme 5.

Figure 5 shows FTD chromatograms of OHEA samples of various MW. It can be seen that, as expected, chromatograms do not depend essentially on the samples' MW. These facts once more testify for chromatography under conditions close to critical ones.

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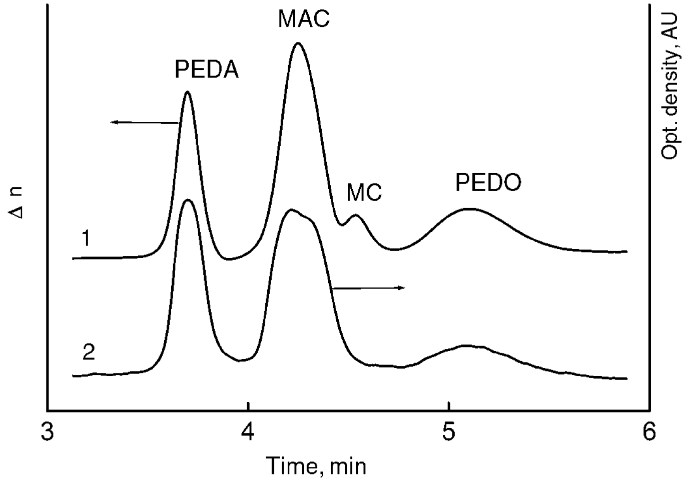
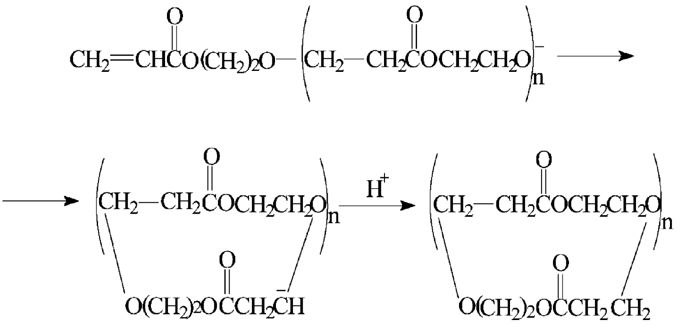


FIGURE 4 Chromatogram of OHEA (the same sample as in Figure 1.). Eluent: MEK/methanol (96/4), 0.7 mL/min, column temperature 60 °C. 1, refractometric trace; 2, UV trace at 215 nm.



SCHEME 5

Thus, a set of chromatographic, spectrophotometric, and mass spectroscopic data provide evidence that peak assignment on FTD chromatograms was made correctly and reflects a real distribution of OHEA over functionality.

Liquid Chromatography of OHEMA Under Critical Conditions

A repeating unit in OHEMA oligomer is less polar than one in OHEA; therefore we expected a weaker eluent to be used for realization of critical

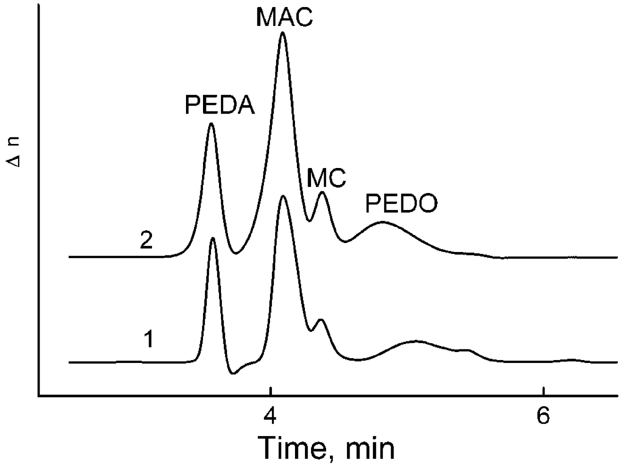


FIGURE 5 FTD chromatograms of OHEA of different molecular weight, M_n: 500 (1) and 1800 (2). Eluent: MEK/methanol, 0.7 mL/min, column temperature 60°C.

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conditions. Actually, chromatograms similar to those for OHEA were obtained upon elution with neat MEK of the products of HEMA polymerization under the action of potassium in tetrahydrofuran (THF). One of such chromatograms is shown in Figure 6.

The essential difference between the chromatograms in Figures 4 and 6 is that for the latter, there are a series of incompletely resolved peaks (denoted as CC) between the peaks of MAC and PEDO. By analyzing the chromatograms of OHEMA samples taken during polymerization, we have shown that the integral intensity of chromatograms decreases and a relative fraction of the peaks located between the peaks of mono- and bifunctional fractions increases with increasing the monomer conversion and oligomer MW. HEMA polymerization can occur over two concurrent ways, i.e., heterochain (similar to HEA) and carbochain via attack of intermediate carbanion on the double bond; see Scheme 6.

Polymerization by carbochain yields branched polymeric molecules with functionality over the hydroxyl groups being coincident with polymerization degree. In this case, the first members of the row (dimers and, apparently, trimers and tetramers) can be eluted under conditions critical for heterochain polymers. Under these conditions, higher carbochain polymer homologies are adsorbed on silica gel practically irreversibly. As

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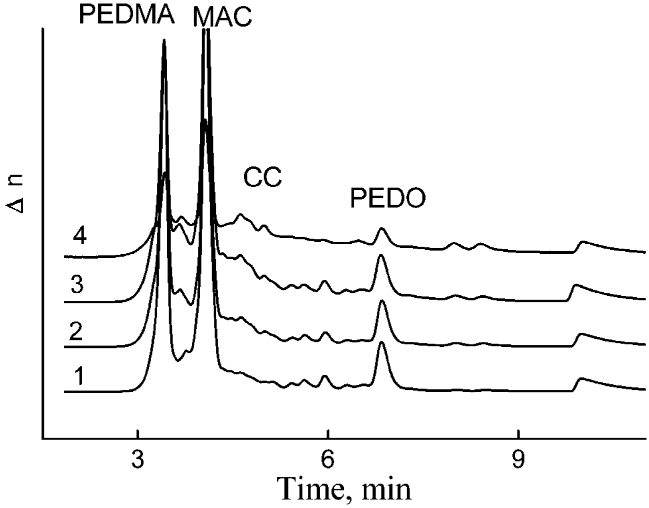
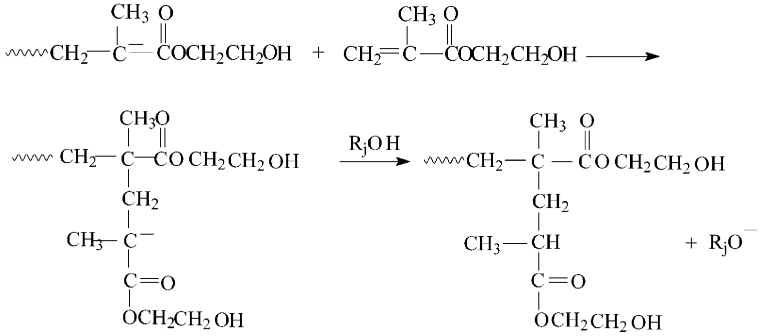


FIGURE 6 Chromatograms of the OHEMA samples in the course of polymerization by action of potassium in THF at 60°C. Reaction time, h: 5 (1), 13 (2), 26 (3), 169 (4). Eluent: MEK, 0.7 mL/min, column temperature 60°C, refractometric detector. Here PEDMA is polyesterdimethacrylates and CC is oligomer fraction containing carbochain fragments.



SCHEME 6

the process develops, heterochain molecules with methacrylate end groups can also become involved in the reaction of carbochain growth, thus reducing their fraction in the reaction products. Of note, no cyclic products were discovered for OHEMA. Accumulation of the products that can be referred to as carbochain oligomers is shown in Figure 6.

Formation of the carbochain fragments was observed also at the deep stages of HEA polymerization by action of potassium in the THF solution. Partial gelation of the reaction mixture took place at these stages of the process. Figure 7 demonstrates the appearance and accumulation of such fragments in the soluble part of the polymerization product. The part of the PEDA fraction is very small on this chromatogram because the greatest part is spent on the cross-linked gel fraction.

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EXPERIMENTAL

Syntheses of Oligomers

Monomers (Aldrich) were purified by vacuum distillation and stabilized by 0.01% of N,N-tetramethyl piperidyl oxyde. Potassium was purified by melting under a layer of boiling tetrahydrofurane in argon atmosphere. Lithium *tert*-butylate was prepared by solution of metal in excess of boiling *tert*-butanol in argon atmosphere, and excess of alcohol was removed by evaporating in vacuum. Polymerization was carried out in block. Temperature of the reaction mixture was kept slightly above the melting point of metal in the case of potassium as the initiator. Potassium was dissolved in the monomer in a few minutes. Lithium *tert*-butylate was added in the monomer as the saturated solution in tetrahydrofurane.

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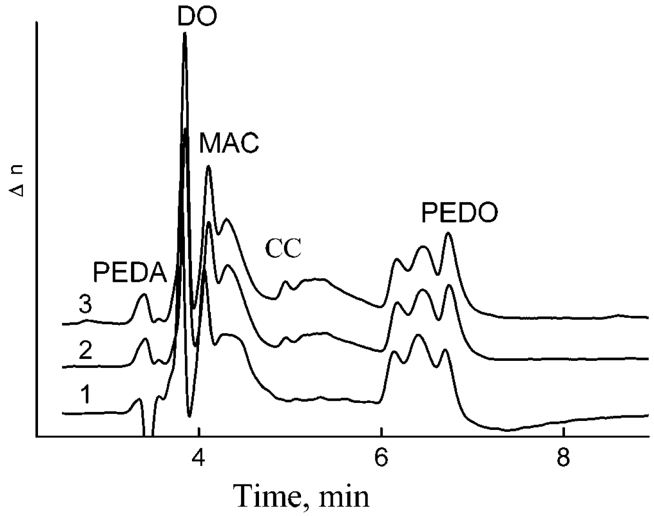

FIGURE 7 FTD chromatograms of OHEA derived by HEA polymerization under the action of potassium in THF at 60°C. Eluent: MEK/DO 85/15, 0.7 mL/min, column temperature 60°C, refractometric detector. Reaction time, min: 40 (1), 60 (2), 85 (3).

Exhaustive acrylation of OHEA was made by treating the oligomer with acryloyl chloride in the presence of triethylamine in the toluene solution.

Chromatographic Technique

Chromatography was carried out by using the Waters chromatograph supplied by the UV-Vis photodiode array detector Waters PDA 996, by the differential refractometric detector Waters DR 410, and by the thermostat for columns. We used the column 250 × 4 mm with Silasorb SPH 600 (5 μ) as sorbent, and eluent rate was 0.7 mL/min. The isocratic mode of elution was used as the basic mode; the double-pump technique with the eluents mixer was applied for preliminary selection of the eluent composition only.

CONCLUSIONS

Chromatography under conditions close to the critical ones is especially useful for studying of functional type distribution of oligomers. Use of this method makes it possible to establish the proceeding of interchain exchange reactions resulting in redistribution of functional end groups at anionic polymerization of 2-hydroxyethy(meth)acrylates.

It was shown that the target reaction of macromonomer formation is accompanied by intense interchain exchange reaction, reaction of macrocycles formation, and slow vinyl polymerization with formation of carbochain fragments. The role of last reaction is increased with conversion. The mechanism of anionic polymerization of 2-hydroxyethy(meth)acrylates is discussed in detail in our previous publications[5–9].

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