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Radical initiators and their influence on the viscosity and molecular weight of acrylic polymers applied in pressure-sensitive adhesives

Summary — Acrylic polymers, which can be applied as pressure-sensitive adhesives (PSA), based on 2-ethylhexyl acrylate, methyl acrylate, and acrylic acid were synthesized in ethyl acetate using azoperoxyester radical initiators. First, the investigated azoperoxyesters were synthesized and isolated. In a second stage, the thermally activated azo groups initiated the radical polymerization of the acrylate monomers. The viscosity, molecular weights, and polydispersities of the synthesized acrylic polymers usable as PSA were evaluated. The newly synthesized radical azoperoxyester initiators were compared with the commercial azo-initiator azobisisobutyronitrile (AIBN).
Key words: radical azoperoxyester initiators, polymerization, synthesis of acrylic PSA, viscosity, molecular weight, polydispersity.

INICJATORY RODNIKOWE I ICH WPŁYW NA LEPKOŚĆ I CIĘŻAR CZĄSTECZKOWY POLIMERÓW POLIAKRYLANOWYCH STOSOWANYCH W ROZPUSZCZALNIKOWYCH KLEJACH SAMOPRZYLEPNYCH
Streszczenie — Opisano syntezę nowych rodnikowych inicjatorów azonadtlenoestrowych. Następnie zsyntetyzowane azonadtlenoestry oraz handlowy inicjator AIBN zastosowano do przeprowadzonej w temperaturze wrzenia rozpuszczalnika rodnikowej polimeryzacji rozpuszczalnikowej wybranych monomerów akrylanowych (akrylanu 2-etyloheksylu, akrylanu metylu oraz kwasu akrylowego). Badano wpływ rodzaju, różniących się budową chemiczną rodnikowych inicjatorów azowych, i ich ilości na lepkość, ciężar cząsteczkowy ($\overline{M_w}$, $\overline{M_n}$) oraz polidyspersyjność (*PDI*) otrzymanych polimerów akrylanowych. Największe wartości lepkości, $\overline{M_w}$ i $\overline{M_n}$ uzyskano w przypadku polimerów otrzymanych z użyciem inicjatora o najdłuższym łańcuchu (AIBN-HEP). Wzrost stężenia inicjatorów w każdym przypadku powodował zmniejszenie tej wartości.
Słowa kluczowe: rozpuszczalnikowe poliakrylanowe kleje samoprzylepne, rodnikowe inicjatory azonadtlenoestrowe, lepkość, ciężar cząsteczkowy, polidyspersyjność.

Bifunctional initiator contains two or more (similar or different) groups in its structure that can initiate the polymerization process *via* strictly defined mechanisms (ionic, radical) [1—4].

Azoperoxy compounds are bifunctional initiators containing azo and peroxy groups showing different thermal or photochemical stability. These groups initiate the polymerization according to free-radical mechanism.

Azoperoxy compounds can be classified as azodialkyl peroxides, azodiacyl peroxides, azoperoxyesters, and azohydroperoxides. The first three groups of compounds can act as bifunctional initiators in the generation of block copolymers, or as simple traditional initiators in the radical polymerization of monomers. Azohydroperoxides, in contrast to the previous ones, cannot be used as bifunctional initiators because of the simultaneous decomposition (to radicals) of both functional groups.

Azodiacyl peroxides and azoperoxyesters were tested as initiators in styrene [5, 6] and acrylamide [7] polymerization processes as well as in the preparation of block copolymers from vinyl [8—10] and acrylic [11] monomers. In the 1980s, an azoperoxy compound [9] was produced by the Ludicol Division of Pennwalt Corporation. This compound, which is no longer on the market, was made from commercially available 4,4'-azo-bis-(4-cyanopentanoic) acid and *tert*-butyl hydroperoxide.

Because of the similar decomposition temperatures of azo and peroxy groups, azoperoxy compounds are not suitable for obtaining well-defined block copolymers when both stages of the polymerization process are initiated thermally. If one of the stages is initiated photochemically, and the other one thermally, nevertheless, the results are satisfactory [12].

Azoperoxy compounds also have some other advantages compared to traditional free-radical initiators (*e.g.*, a higher initiation rate) [13]. Previously reported azoperoxy compounds were mostly formed in reactions of azo
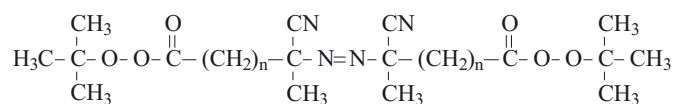
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compounds (usually acid chlorides) [6, 8, 10] with peroxy compounds (hydroperoxides and peracids) in both heterogenic and homogenic systems.

The compounds described herein belong to the azoperoxyester family and are composed of three labile groups, namely, an azo group and two peroxy groups, which are separated by carbon chains with different numbers of methylene groups [mostly from two to four, see Formula (1)].

$$
\begin{array}{c}
\text{CH}_3 \quad\quad\ \text{O} \quad\quad\quad\quad \text{CN} \quad\ \text{CN} \quad\quad\quad\quad \text{O} \quad\quad\ \text{CH}_3 \\
\text{H}_3\text{C}-\overset{|}{\underset{|}{\text{C}}}-\text{C}-\text{O}-\text{O}-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_n-\overset{|}{\underset{|}{\text{C}}}-\text{N}{=}\text{N}-\overset{|}{\underset{|}{\text{C}}}-(\text{CH}_2)_n-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{O}-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3 \\
\text{CH}_3 \quad\quad\quad\quad\quad\quad \text{CH}_3 \ \ \text{CH}_3 \quad\quad\quad\quad\quad \text{CH}_3
\end{array}
$$

n = 2, 3, 4 $\hspace{6cm}$ (I)

Earlier, azoperoxyesters were prepared by esterification of azo acid chlorides with *tert*-butyl hydroperoxide [14] in a heterogenic system. A simpler method to obtain azoperoxyesters is described herein.

EXPERIMENTAL

Materials

— Three carboxylic acids containing azofunctional groups were used for syntheses of azoperoxyesters: 4,4'-azobis(4-cyanopentanoic) acid (Fluka), 5,5'-azobis(5-cyanohexanoic) acid, and 6,6'-azobis(6-cyanoheptanoic) acid. Last two acids were synthesized by Zawadiak and co-workers as described in [11].

— Tetrahydrofuran (THF) was distilled over metallic Na and used immadiately.

— *Tert*-butyl hydroperoxide (Merck) was washed with hexane.

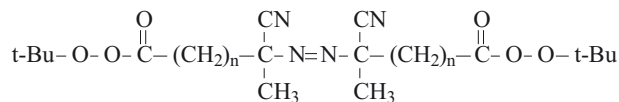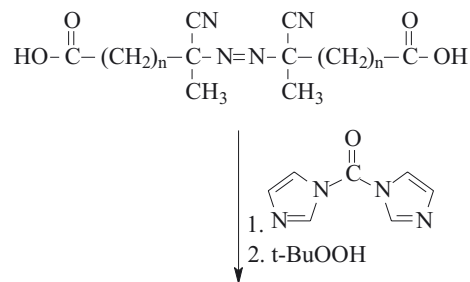— 1,1'-Carbonyldiimidazole (Alfa Aestar) was used as supplied.

— For the syntheses of solvent-borne acrylic polymers applied in pressure-sensitive adhesives (PSAs) three acrylate monomers (obtained from BASF, Germany): 2-ethylhexyl acrylate, methyl acrylate, and acrylic acid were used.

— Azobisisobutyronitrile (AIBN) was supplied by Degussa.
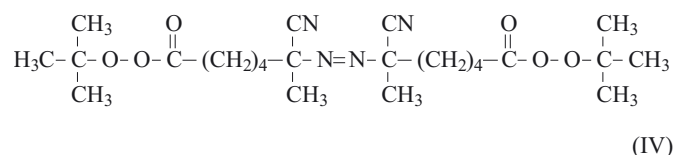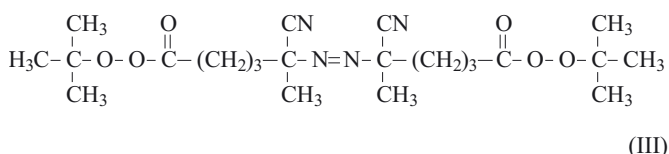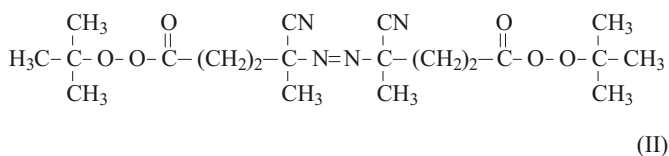
Syntheses of azeoperoxyester radical initiators

The proposed method for syntheses of azoperoxyesters consists of a single-step reaction, presented in Scheme A, between a carboxylic-acid compound containing an azo functional group and *tert*-butyl hydroperoxide, in the presence 1,1'-carbonylimidazole.

A carboxylic acid (10 mmol), containing an azo functional group dissolved in dry THF was introduced into a three-necked round-bottom (3-RB) flask equipped with a mechanic stirrer, a nitrogen supply, and a dropping funnel. A solution of 1,1'-carbonyldiimidazole

$$
\begin{array}{c}
\text{O} \quad\quad\quad \text{CN} \quad\quad \text{CN} \quad\quad\quad\ \text{O} \\
\text{HO}-\overset{\|}{\text{C}}-(\text{CH}_2)_n-\overset{|}{\underset{|}{\text{C}}}-\text{N}{=}\text{N}-\overset{|}{\underset{|}{\text{C}}}-(\text{CH}_2)_n-\overset{\|}{\text{C}}-\text{OH} \\
\quad\quad\quad\quad\quad \text{CH}_3 \quad\quad\ \text{CH}_3
\end{array}
$$

1.
2. t-BuOOH

$$
\begin{array}{c}
\text{O} \quad\quad\quad\quad \text{CN} \quad\quad \text{CN} \quad\quad\quad\ \text{O} \\
\text{t-Bu}-\text{O}-\text{O}-\overset{\|}{\text{C}}-(\text{CH}_2)_n-\overset{|}{\underset{|}{\text{C}}}-\text{N}{=}\text{N}-\overset{|}{\underset{|}{\text{C}}}-(\text{CH}_2)_n-\overset{\|}{\text{C}}-\text{O}-\text{O}-\text{t-Bu} \\
\quad\quad\quad\quad\quad\quad\ \text{CH}_3 \quad\quad\ \text{CH}_3
\end{array}
$$

Scheme A. Synthesis of the azoperoxyester radical initiator

(21 mmol) in dry THF was added to this mixture. The suspension was then vigorously stirred for about 30 min. After this time, the mixture was cooled to a temperature below 5 °C, and *tert*-butyl hydroperoxide (35 mmol) was added.

$$
\begin{array}{c}
\text{CH}_3 \quad\quad\ \text{O} \quad\quad\quad \text{CN} \quad\ \text{CN} \quad\quad\quad \text{O} \quad\quad\ \text{CH}_3 \\
\text{H}_3\text{C}-\overset{|}{\underset{|}{\text{C}}}-\text{O}-\text{O}-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_2-\overset{|}{\underset{|}{\text{C}}}-\text{N}{=}\text{N}-\overset{|}{\underset{|}{\text{C}}}-(\text{CH}_2)_2-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{O}-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3 \\
\text{CH}_3 \quad\quad\quad\quad\quad\quad \text{CH}_3 \ \ \text{CH}_3 \quad\quad\quad\quad\ \text{CH}_3
\end{array}
$$

$\hspace{7cm}$ (II)

$$
\begin{array}{c}
\text{CH}_3 \quad\quad\ \text{O} \quad\quad\quad \text{CN} \quad\ \text{CN} \quad\quad\quad \text{O} \quad\quad\ \text{CH}_3 \\
\text{H}_3\text{C}-\overset{|}{\underset{|}{\text{C}}}-\text{O}-\text{O}-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_3-\overset{|}{\underset{|}{\text{C}}}-\text{N}{=}\text{N}-\overset{|}{\underset{|}{\text{C}}}-(\text{CH}_2)_3-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{O}-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3 \\
\text{CH}_3 \quad\quad\quad\quad\quad\quad \text{CH}_3 \ \ \text{CH}_3 \quad\quad\quad\quad\ \text{CH}_3
\end{array}
$$

$\hspace{7cm}$ (III)

$$
\begin{array}{c}
\text{CH}_3 \quad\quad\ \text{O} \quad\quad\quad \text{CN} \quad\ \text{CN} \quad\quad\quad \text{O} \quad\quad\ \text{CH}_3 \\
\text{H}_3\text{C}-\overset{|}{\underset{|}{\text{C}}}-\text{O}-\text{O}-\overset{\text{O}}{\overset{\|}{\text{C}}}-(\text{CH}_2)_4-\overset{|}{\underset{|}{\text{C}}}-\text{N}{=}\text{N}-\overset{|}{\underset{|}{\text{C}}}-(\text{CH}_2)_4-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{O}-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3 \\
\text{CH}_3 \quad\quad\quad\quad\quad\quad \text{CH}_3 \ \ \text{CH}_3 \quad\quad\quad\quad\ \text{CH}_3
\end{array}
$$

$\hspace{7cm}$ (IV)

After 5 hour reaction time, Et$_2$O was added to the mixture and stirring was continued for about 45 min. The mixture was then washed twice (with 5 % NaOH and water), and the organic layer was dried using anhydrous MgSO$_4$. The solvent was finally removed in a vacuum evaporator at ambient temperature. All prepared azoperoxyesters di-*tert*-butyl-4,4'-azobis(4-cyanoperoxypentanoate), di-*tert*-butyl-5,5'-azobis(5-cyanoperoxyhexanoate), and di-*tert*-butyl-6,6'-azobis(6-cyanoperoxyheptanoate) [Formulas (II)—(IV), respectively].

Syntheses of acrylic polymers

The solvent-borne acrylic polymers applied in PSAs were synthesized using 2-ethylhexyl acrylate (60 wt. %), methyl acrylate (33 wt. %), and acrylic acid (7 wt. %) at the boiling temperature of the solvent (ethyl acetate) in

the presence of 0.1—1.0 wt. % of AIBN or one of synthesized azoperoxyesters. The polymerization process was run for 6 h to reach a 50 wt. % acrylic polymer content [15].

Methods of testing

The progress of the reaction of synthesis of azoperoxyester was followed using thin layer chromatography (TLC), mobile phase: CH_2Cl_2:CH_3COCH_3 = 9:1; a solution of sodium iodide in acetic acid was used to visualize the separated substances.

Synthesized azoperoxyesters were analyzed by ^1H NMR and IR methods. ^1H NMR spectra were recorded in $CDCl_3$ using a Varian Unity Inova-300 spectrometer [using tetramethylsilane (TMS) as the internal standard] and compared with a reference standard. IR spectra were recorded using Zeiss Specord M 80 spectrometer.

The yields of reactions of synthezes of azoperoxyesters were determined according to the gravimetric method and calculated for the pure compounds.

Effects of the kind and amount of novel azoperoxyesters used as radical initiators on the viscosity, molecular weight and polydispersity of synthesized solvent-borne acrylic polymers were investigated [16]. The viscosity was determined at 23 ᵒC using a Rheomat RM 189 (with spindle No. 3), from Rheometric Scientific.

Molecular weight studies were performed in THF using a liquid chromatography LaChrom system (RJ Detector: L-7490, LaChrom UV Detector: L-7400 from Merck-Hitachi) equipped with a PLgel 106-Å column from Hewlett-Packard.

RESULTS AND DISCUSSION

Azoperoxyesters

Azoperoxyesters were obtained in a single-step reaction. This method is simpler than the double-step method described in [14], because individual processes preparation and separation of acylating agent (acid chloride) are not needed. The double-step procedure was used earlier for the syntheses of esters and peroxyesters [17]. Higher yields of the desired compounds were achieved by using an excess of hydroperoxide.

In the method proposed here, the acylating agent is generated *in situ* by reaction of 1,1'- carbonyldiimidazole with an azo-functionalized carboxylic acid thereby being immediately coupled to hydroperoxide. The yields of compounds, listed in Table 1, obtained in this way are higher than those achieved in the double-step reaction, with the purity of products being comparable. All compounds were characterized by comparison of their spectra with that of a reference standard.

A big disadvantage of the proposed method, however, is the sensitivity of both 1,1'-carbonyldiimidazole

and the generated acylating agent to traces of water. The presence of water causes the decomposition of these compounds. Although the azo acid chlorides used in the two-step method are also sensitive to water, but less sensitive, because the hydrolysis of these compounds proceeds much more slowly.

T a b l e 1. **Yields of reactions of synthezes of azoperoxyesters**

Compound	Yield, %
di-*tert*-butyl-4,4'-azobis(4-cyanoperoxypentanoate)	83
di-*tert*-butyl-5,5'-azobis(5-cyanoperoxyhexanoate)	78
di-*tert*-butyl-6,6'-azobis(6-cyanoperoxyheptanoate)	75

Influence of kind and concentration of azoperoxyesters on the properties of acrylic polymers

The effects of the kind and concentration (from 0.1 to 1.0 wt. %) of azoperoxyesters on the viscosity, molecular weights and polydispersity of synthesized solvent-borne acrylic polymers used as PSAs present experimental data listed in Table 2.

T a b l e 2. **Viscosity, molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and polydispersity (*PDI*) of synthesized acrylic polymers applied in PSAs, prepared with use of AIBN or tested azoperoxyester initiators**

Concentration of azoperoxyester, wt. %	Polymer viscosity mPa · s	$\overline{M}_w$	$\overline{M}_n$	*PDI*
2,2'-azobisdiisobutyronitrile (AIBN)				
0.1	13 500	712 000	197 000	3.61
0.3	4900	505 000	113 000	4.47
0.5	3800	423 000	91 000	4.65
0.8	2600	378 000	77 300	4.89
1.0	1800	315 000	61 500	5.12
di-*tert*-butyl-4,4'-azobis(4-cyanoperoxypentanoate) (AIBN-PEN)				
0.1	26 500	874 000	271 000	3.23
0.3	19 900	833 000	252 000	3.31
0.5	13 100	707 000	206 000	3.44
0.8	10 000	664 000	183 000	3.62
1.0	8600	622 000	161 000	3.86
di-*tert*-butyl-5,5'-azobis(5-cyanoperoxyhexanoate) (AIBN-HEX)				
0.1	30 100	880 000	277 000	3.18
0.3	23 000	852 000	259 000	3.29
0.5	18 700	806 000	238 000	3.39
0.8	16 100	755 000	213 000	3.54
1.0	13 700	712 000	191 000	3.72
di-*tert*-butyl-6,6'-azobis(6-cyanoperoxyheptanoate) (AIBN-HEP)				
0.1	31 300	883 000	287 000	3.08
0.3	25 800	865 000	273 000	3.17
0.5	22 200	842 000	262 000	3.21
0.8	18 600	801 000	241 000	3 32
1.0	16 400	765 000	218 000	3.51

The viscosity values of the synthesized acrylic polymers are shown in Figure 1. Value of this property strongly depends on the kind and concentration of the corresponding azoperoxyester radical initiator. In general, the viscosity decreases with increasing concentration of each radical initiator. During polymerization, large amounts of free radicals are produced, thus reducing the viscosity of the obtained polymer with self-adhesive properties.

Figure 2 shows the influence of kind and concentration of initiator on the weight-average molecular weight ($\overline{M_w}$) of the synthesized polymer. As it was expected after evaluating the viscosity, the increase amounts of every tested initiator corresponds to a decrease in $\overline{M_w}$ value. The highest $\overline{M_w}$ was achieved with use of 0.1 wt. % of AIBN-HEP as the radical initiator.

The influence of type and concentration of azoperoxyester compound on the number-average molecular weight ($\overline{M_w}$) of the synthesized solvent-borne acrylic polymer is illustrated in Figure 3. As can be seen, the efficiency of investigated initiator clearly depends on both its chemical structure (expressed as the length of the azoperoxyester molecule) and the concentration. The longer the azoperoxyester molecule, the greater value of $\overline{M_n}$ (AIBN-HEP).

Higher molecular weight acrylic polymers allow to manufacture the cohesive layers while lower molecular weight ones are suitable for production of adhesive and tacky layers. Polydispersity of synthesized polymers, expressed as molecular weight distribution, includes information about their performance. Increasing dispersity ameliorates tacking and peel adhesion while negatively influences the shear strength. On the contrary, a decrease in polydispersity ($PDI = \overline{M_w}/\overline{M_n}$) improves the shear strength but affects the adhesive performance.

Figure 4 shows PDI values of the synthesized acrylic polymers as functions of the concentrations of new azoperoxyester initiators. The use of AIBN allows to synthesize the solvent-borne acrylic polymers with relatively wide polydispersity whereas the introduction of novel
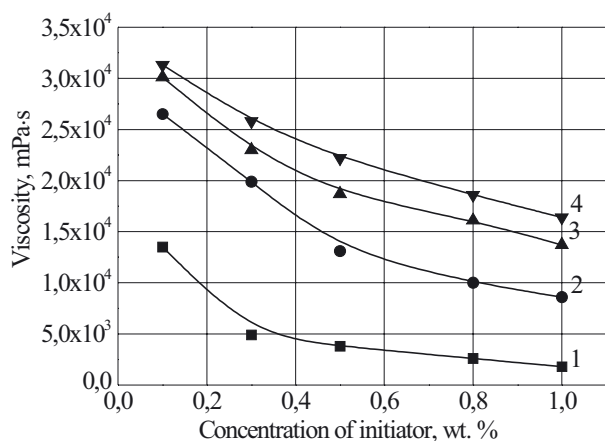

Fig. 1. Effects of the type and concentration of initiator on the viscosity of acrylic polymer: 1 — AIBN, 2 — AIBN-PEN, 3 — AIBN-HEX, 4 — AIBN-HEP
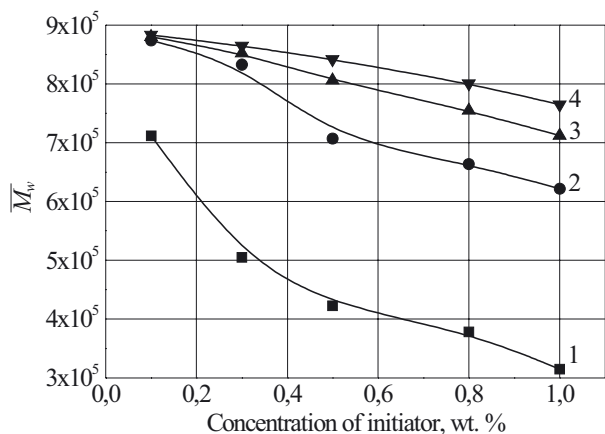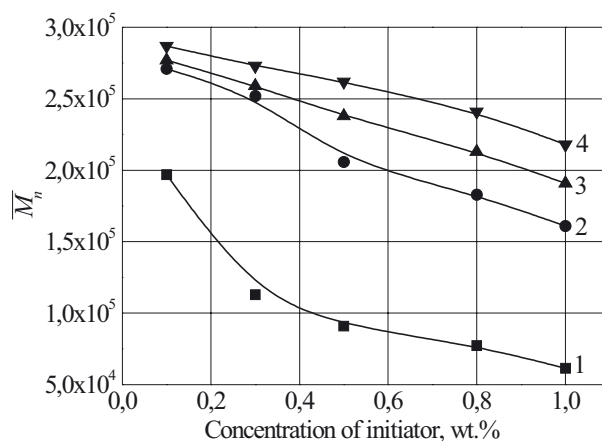

Fig. 3. Effects of the type and concentration of initiator on the molecular weight ($\overline{M_n}$) of acrylic polymer: 1 — AIBN, 2 — AIBN-PEN, 3 — AIBN-HEX, 4 — AIBN-HEP

Fig. 2. Effects of the type and concentration of initiator on the molecular weight ($\overline{M_w}$) of acrylic polymer: 1 — AIBN, 2 — AIBN-PEN, 3 — AIBN-HEX, 4 — AIBN-HEP
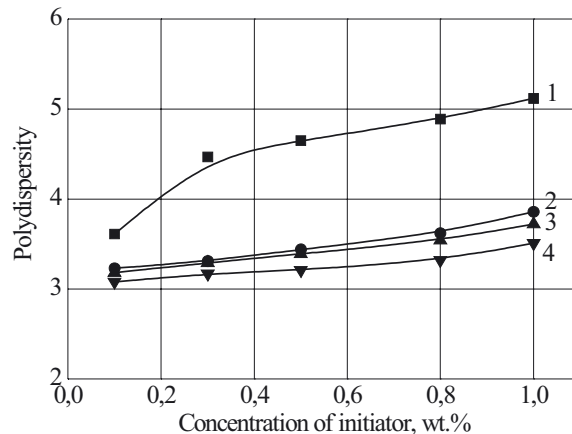

Fig. 4. Effects of the type and concentration of initiator on the polydispersity of acrylic polymer: 1 — AIBN, 2 — AIBN--PEN, 3 — AIBN-HEX, 4 — AIBN-HEP

azoperoxyester initiators let produce the acrylic polymers with relatively small polydispersity, what is typical for acrylic polymers used as PSAs characterized by high cohesion level [18].

CONCLUSIONS

Azoperoxyester initiators comparable with AIBN have recently attracted considerable attention because of their potential industrial applications in the development of high-performance self-adhering technical and medical articles. High-performance solvent-borne acrylic polymers, which can be applied in pressure-sensitive adhesives were obtained by the radical polymerization of typical acrylate monomers using the novel azoperoxyester initiators instead of AIBN.

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