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Acrylic monomers and polymers with pyrimidine rings

RAPID COMMUNICATION

Summary — Acrylates and methacrylates with pyrimidine rings were synthesized starting from 1,3-bis(hydroxyalkyl) 5,5-diethylbarbiturates and acrylic or methacrylic acids. Then these monomers containing pyrimidine rings were subjected to radical polymerization. The values of thermal stability of the polymers were enhanced in comparison with those of common polyacrylates and polymethacrylates obtained from aliphatic diols.

Key words: acrylates with pyrimidine rings, methacrylates with pyrimidine rings, radical polymerization, thermal properties.

MONOMERY I POLIMERY AKRYLOWE Z PIERŚCIENIAMI PIRYMIDYNOWYMI

Streszczenie — W reakcjach kwasów akrylowego lub metakrylowego z odpowiednimi 5,5-dietylobarbituranami 1,3-bis(2-hydroksyalkilowymi) zsyntetyzowano monomery akrylowe lub metakrylowe zawierające pierścienie pirymidynowe (tabela 1). Otrzymane monomery poddano polimeryzacji w obecności nadtlenu benzoilu jako inicjatora. Skaningowa kalorymetria różnicowa (DSC) wykazała, że uzyskane polimetakrylany charakteryzują się temperaturą zeszklenia (T_g) wyższą niż 200 °C (tabela 2). Z analizy termicznej wynika, że poliakrylany i polimetakrylany z pierścieniami pirymidynowymi wykazują zwiększoną odporność termiczną w porównaniu z klasycznymi, alifatycznymi poliakrylanami i polimetakrylanami. Temperatura maksymalnego rozkładu niektórych z nich wynosi 420—430 °C.

Słowa kluczowe: akrylany z pierścieniem pirymidynowym, metakrylany z pierścieniem pirymidynowym, polimeryzacja rodnikowa, właściwości termiczne.

Incorporation of 1,3,5-triazine, perhydrotriazine, purine and carbazole rings into the polymers results in their increased thermal stability [1, 2]. Recently we have found that introduction of pyrimidine rings into urethane oligomers also increased their thermal stability in comparison with traditional polyurethanes [3]. The oligomers were obtained from diols containing pyrimidine rings and suitable diisocyanates. The data concerning the methods of syntheses of acrylate or methacrylate monomers with pyrimidine rings or their polymers are reported here for the first time. Previously we have demonstrated that the precursor diols can be obtained from 5,5-diethylbarbituric acid and ethylene or propylene oxides or ethylene or propylene carbonates [4].

EXPERIMENTAL

Materials

1,3-bis(2-hydroxyethyl) 5,5-diethylbarbiturate (BHEDEB) and 1,3-bis(2-hydroxypropyl) 5,5-diethylbarbiturate (BHPDEB) were obtained as it was described

previously [4]. The acrylic and methacrylic acids [pure, delivered by Aldrich (UK)] were distilled prior to use. Benzoyl peroxide (pure) was supplied by POCh (Poland).

Syntheses of acrylates and methacrylates with pyrimidine rings

0.05 Mole of BHEDEB (13.6 g) or BHPDEB (15.0 g) and 0.13 mole of methacrylic (11.9 g) or acrylic acid (9.4 g) were placed in three-necked 250 cm³ flask equipped with Dean-Stark head and reflux condenser. Then 120 cm³ of toluene solvent and 1.0—2.0 cm³ of concentrated sulfuric acid, used as catalyst, were added and the mixture was heated to reflux (110—115 °C) followed by azeotropic water removal with toluene. The reactions were conducted in the presence of 2 % phenothiazine in order to prevent polymerization of unsaturated acids. After the esterification reaction was completed the mixture was washed with 10 % aqueous solution of potas-

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sium carbonate until evolution of gas ceased, then with water and finally the organic solvents were removed under vacuum to get resin product, which was further purified by high-vacuum distillation ($t = 120\text{--}180\text{ }^{\circ}\text{C}$, $p = 0.7 \cdot 10^{-3}\text{ MPa}$) prior to use.

Syntheses of polyacrylates and polymethacrylates with pyrimidine rings

In a sealed 20 cm^3 glass ampoule 0.01 mole of one of monomers synthesized was placed and 0.5—1 g of benzoyl peroxide per 100 g of ester was added. Ester was mixed with initiator until the mixture became homogeneous, then the mixture was flushed with nitrogen and the ampoule was sealed and heated for 4 hours at temp. $80\text{ }^{\circ}\text{C}$. The colorless, crosslinked polymers without pores

were obtained. The products were not soluble in common organic solvents.

Methods of testing

Thermal analyses of polymers were performed in ceramic crucible at $20\text{--}1000\text{ }^{\circ}\text{C}$ temperature range, with 100 min registration time, 200 mg sample, 10 deg/min heating rate under an air atmosphere with Paulik-Paulik-Erdey derivatograph (MOM, Hungary).

DSC studies were done using a DSC 822^e Mettler Toledo calorimeter at $20\text{--}300\text{ }^{\circ}\text{C}$ temperature range, 10 deg/min heating rate, 10—20 mg samples under nitrogen atmosphere.

The ^1H NMR and ^{13}C NMR spectra of products were recorded using a 500 MHz Bruker UltraShield in

Table 1. Analytical data of acrylates and methacrylates with pyrimidine rings

Compound	R1 and R' in eq. (1)	Yield %	Ref. index n_D^{20}	Elemental analysis		^1H NMR, ppm	^{13}C NMR, ppm	IR, cm^{-1}
				calculated	found			
DTPDEDA	R = H R' = -CH=CH ₂	60	1.4895	C 56.84; H 6.31; N 7.36	C 56.62; H 6.32; N 7.52	(d ₆ -acetone), 0.8 (6H, t, CH ₂ -CH ₃), 1.95 (4H, q, CH ₂ -CH ₃), 4.2 (4H, t, CH ₂ -O), 4.3 (4H, t, N-CH ₂), 5.9—6.3 (CH=CH ₂)	(d ₆ -a-cetone), 8.9 (C ₅ -CH ₂ -CH ₃), 32.1 (C ₅ -CH ₂ -CH ₃), 43.3 (N-CH ₂), 57.3 (C ₅), 61.1 (CH ₂ O), 127.9 (CH=), 131.7 (CH ₂ =), 150.2 (C ₂), 165.2 (COO), 171.0 (C ₄ , C ₆)	3037 (CH ₂ =), 2971 (CH ₂), 1725 (C=O in ester), 1675 (C=O in ring), 1635 (C=C), 1437 (CH ₂), 1397 (C-N), 1293, 1262 (CO-O), 1174 (C-N), 1068 (C-O), 808 (N-C=O)
DTPDEDM	R = H R' = -C(CH ₃)=CH ₂	54	1.4702	C 58.80; H 6.86; N 6.86	C 58.36; H 6.36; N 6.82	(d ₆ -acetone), 0.8 (6H, t, CH ₂ -CH ₃), 1.9 (6H, s, =C-CH ₃), 1.95 (4H, m, CH ₂ -CH ₃), 4.2 (4H, t, CH ₂ -O), 4.4 (4H, t, N-CH ₂ -), 5.6, 6.1 (2H, 2d, =CH ₂)	(d ₆ -acetone), 9.5 (C ₅ -CH ₂ -CH ₃), 18.4 (CH ₃ C=), 33.5 (C ₅ -CH ₂ -CH ₃), 41.4 (N-CH ₂), 58.8 (C ₅), 62.5 (CH ₂ O), 125.7 (CH ₂ =), 137.5 (C=), 151.7 (C ₂), 167.3 (COO), 172.2 (C ₄ , C ₆)	2844—2966 (CH ₃ , CH ₂ , CH ₂ =), 1720 (C=O in ester), 1686 (C=O in ring), 1634 (C=C), 1435 (CH ₂), 1398 (C-N), 1298 (CO-O), 1152 (C-O), 943 (=CH), 808 (N-C=O)
DTPDPDA	R = CH ₃ R' = -CH=CH ₂	49	1.4989	C 58.82; H 6.86; N 6.86	C 58.96; H 6.91; N 7.09	(d ₆ -DMSO), 0.7 (6H, m, CH ₂ -CH ₃), 1.3 (6H, m, CH-CH ₃), 1.8 (4H, m, CH ₂ -CH ₃), 3.9, 4.2 (4H, m, N-CH ₂), 5.1 (4H, m, CH-O and CH=), 5.9—6.2 (4H, m, CH ₂ =)	(d ₆ -acetone), 8.7 (C ₅ -CH ₂ -CH ₃), 17.5 (CH ₃ -CH-O), 31.8 (C ₅ -CH ₂ -CH ₃), 45.0 (N-CH ₂), 57.2 (C ₅), 68.3 (COO-CH), 128.2 (CH=), 131.6 (CH ₂ =), 150.4 (C ₂), 164.9 (COO), 170.9 (C ₄ , C ₆)	2972—2881 (CH ₂ =, CH ₃ , CH ₂ , CH), 1722 (C=O in ester), 1681 (C=O in ring), 1638 (C=C), 1521 (ring vibration), 1435 (CH ₂), 1400 (C-N), 1383 (CH ₃), 1291, 1266 (CO-O), 1191 (C-N), 1067, 1050 (C-O), 985, 809 (N-C=O), 942 (CH ₂ =)
DTPDPDM	R = CH ₃ R' = -C(CH ₃)=CH ₂	48	1.4740	C 60.27; H 7.76; N 6.39	C 60.02; H 7.92; N 6.51	(d ₆ -DMSO), 0.7 (6H, m, CH ₂ -CH ₃), 1.3 (6H, m, CH-CH ₃), 1.8 (10H, m, =C-CH ₃ , CH ₂ -CH ₃), 4.2 (4H, m, N-CH ₂), 5.1 (2H, m, CH-O), 5.1, 5.8 (4H, m, CH ₂ =)	(d ₆ -DMSO), 8.9 (C ₅ -CH ₂ -CH ₃), 17.5 (CH ₃ -CH-O), 18.2 (CH ₃ C=), 32.0 (C ₅ -CH ₂ -CH ₃), 43.3 (N-CH ₂), 57.2 (C ₅), 68.3 (COO-CH), 125.9 (CH ₂ =), 137.6 (C=), 150.0 (C ₂), 167.8 (COO), 170.6 (C ₄ , C ₆)	3084 (CH ₂ =), 2966—2877 (CH ₃ , CH ₂ , CH), 1718 (C=O in ester), 1684 (C=O in ring), 1644 (C=C); 1529 (ring vibration), 1435 (CH ₂), 1397 (C-N), 1072, 1063 (C-O), 991 (N-C=O); 930 (CH ₂ =)

DMSO- d_6 with hexamethyldisiloxane as internal standard.

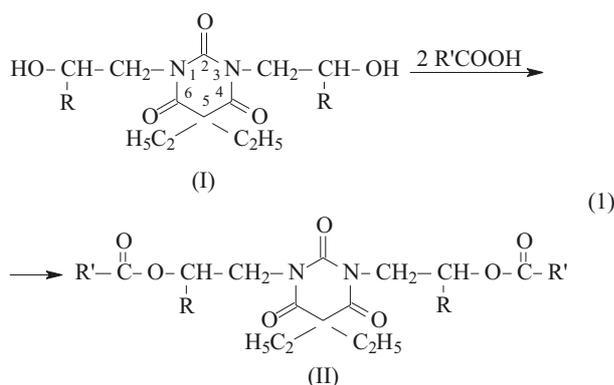
IR spectra (capillary film) of the products were recorded using a Specord 71 IR, Carl Zeiss and PARAGON 1000 FTIR Perkin Elmer spectrometers.

Elemental analyses of acrylates and methacrylates were performed using EA 1108 Carlo-Erba analyzer.

The refractive indices of monomers were determined using Abbe refractometer.

RESULTS AND DISCUSSION

The syntheses of acrylates and methacrylates were performed according to the schematic reactions:



where: R = H- or CH₃-, R' = CH₂=CH- or CH₂=C(CH₃)-

Four types of monomers are obtained:

- 2,2'-(5,5-diethyl-2,4,6-trioxypyrimidine)diethyl diacrylate (DTPDEDA),
- 2,2'-(5,5-diethyl-2,4,6-trioxypyrimidine)diethyl dimethacrylate (DTPDEDM),
- 2,2'-(5,5-diethyl-2,4,6-trioxypyrimidine)dipropyl diacrylate (DTPDPDA),
- 2,2'-(5,5-diethyl-2,4,6-trioxypyrimidine)dipropyl dimethacrylate (DTPDPDM).

The yield of monomers syntheses related to 1,3-bis(2-hydroxyalkyl) 5,5-diethylbarbiturates (BHEDEB or BHPDEB) and spectral characterization of products are collected in Table 1.

When stoichiometric 1:2 amounts of BHEDEB or BHPDEB and acrylic or methacrylic acid were used,

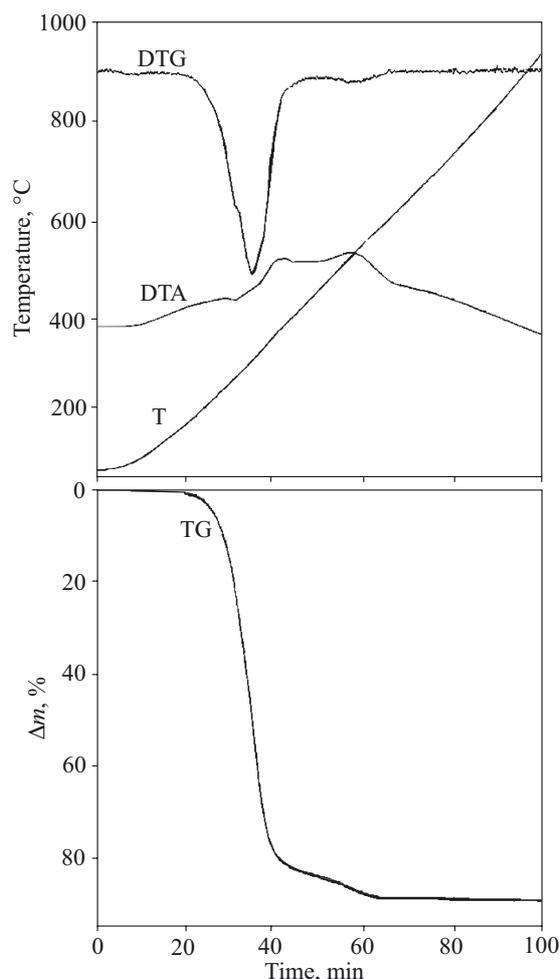


Fig. 1. Results of thermal analysis of poly(DTPDPDM)

some of BHEDEB or BHPDEB were left unreacted as identified by IR [the band 3000 cm⁻¹ of ν(O-H)] and ¹H NMR spectral monitoring. Therefore slight excess of the acid related to BHEDEB or BHPDEB (1.3 mole/mole per OH group) was necessary to increase the yield of ester. The acrylates and methacrylates with pyrimidine rings were radically polymerized with benzoyl peroxide initiator. The results of thermal analyses of polymers obtained are listed in Table 2 and exemplary DTA, DTG and TG curves for poly(DTPDPDM) are presented in Figure 1. DSC analyses of methacrylate polymers

Table 2. Thermal stability and heat resistance of polyacrylates and polymethacrylates with pyrimidine rings determined by thermoanalytical measurements

Entry	Polymer	Temperature of maximum decomposition, °C	T _{5%} , °C	T _{10%} , °C	T _{20%} , °C	T _{50%} , °C	T _g , °C
1	poly(DTPDEDA)	300	238	245	270	320	20–24
2	poly(DTPDEDM)	420	200	220	250	350	>200
3	poly(DTPDPDA)	430	335	360	390	420	104–108
4	poly(DTPDPDM)	315	230	250	270	315	>200
10	poly(methyl acrylate)	—	—	—	—	328 [7]	6 [7]
11	poly(methyl methacrylate)	210–260	—	—	—	283 [8]	105 [7]

[poly(DTPDEDA) and poly(DTPDPDM)] indicated glass transition temperature (T_g) of products at above 200 °C, while poly(DTPDEDA) (obtained from DEBBHE) showed T_g at 20—24 °C, and poly(DTPDPDA) (obtained from DEBBHP) gave T_g at 104—108 °C. These are higher in comparison with $T_g = 6$ °C of classic poly(methyl acrylate). Results of DTA, DTG and TG analyses confirmed enhanced thermal stability of polymethacrylates with pyrimidine rings (Table 2, Figure 1) in comparison with corresponding polymers without such rings [5, 6]. The maximum decomposition temperatures of these products are higher than those of classic poly(methyl acrylate) irrespective the kind of 1,3-bis(2-hydroxyalkyl) 5,5-diethylbarbiturate. The 50 % weight loss of classic poly(methyl acrylate) and poly(DTPDEDA) occurs at similar temperature, while the same 50 % weight loss in case of poly(DTPDPDA) occurs at temperature about 100 °C higher.

CONCLUSIONS

— The method of syntheses of acrylate and methacrylate monomers with pyrimidine rings by esterification of hydroxyalkyl derivatives of 5,5-diethylbarbituric acid and acrylic or methacrylic acid was presented.

— The ester monomers were used to obtain polymers in the reaction of radical polymerization. It has been found that the polymers with pyrimidine rings showed enhanced thermal stability and heat resistance.

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