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MACROMOLECULAR CHEMISTRY
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Synthesis and Thermal Transformations of Bis[4-(1-hydroxyethyl)phenyl] Ether Dimethacrylate

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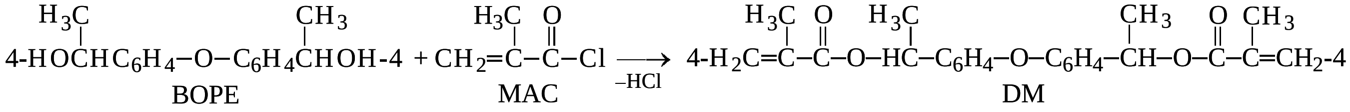
Abstract—Thermal curing of bis[4-(1-hydroxyethyl)phenyl] ether dimethacrylate was studied.

Processing of thermoreactive resins into heat-resistant polymeric materials involves a serious problem: For curing to be efficient, the curing temperature T_c should be maintained higher than the glass transition point T_g of the system being cured. In the highly viscous medium of a thickly cross-linked polymeric matrix at a temperature below T_g, curing drastically decelerates, because transport of reactants to the reaction zone becomes severely hindered. Participation of adjacent functional groups in polymer-analogous transformations might eliminate this problem [1–3].

Being a polyfunctional monomer, bis[4-(1-hydroxyethyl)phenyl] ether dimethacrylate (DM) may be of considerable interest in this respect. It is a component of Rolivsans, novel heat-resistant thermoreactive resins used in modern engineering [4–6]. Owing to the presence of unsaturated methacrylate groups, it is involved in common three-dimensional (3D) polymerization, forming network polymers similar to the well-known diol methacrylates [7–9]. However, a specific feature of DM is the presence of latent ("sleeping") fragments $–C_6H_4–CH(CH_3)–O–CO–$, allowing high-temperature rearrangement of the initial polymeric network of DM in the course of further curing at elevated temperatures. In this study, we analyzed the mechanism of thermal transformations of DM and the structure and properties of the cured products.

Bis[4-(1-hydroxyethyl)phenyl] ether dimethacrylate is formed in synthesis of Rolivsan MV-1, which is a monomer–oligomer compound prepared chemically, i.e., by transformations of a secondary aromatic diol, bis[4-(1-hydroxyethyl)phenyl] ether (BOPE), in the presence of methacrylic acid (MAA), catalyzed with strong mineral acids [10–14]. Pure DM was prepared for the first time by acylation of BOPE with methacryloyl chloride (MAC) [12, 13]. According to ozonolysis data, the content of double bonds in DM is 0.504 mol per 100 g; ester number, 272 mg KOH per gram; n_D^{20}, 1.5410; gelation time at 150°C, 2 min.



$$\underset{\text{BOPE}}{4\text{-HO}\overset{H_3C}{\overset{|}{C}}HC_6H_4{-}O{-}C_6H_4\overset{CH_3}{\overset{|}{C}}HOH\text{-}4} + \underset{\text{MAC}}{CH_2{=}\overset{H_3C}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Cl} \xrightarrow[-HCl]{} \underset{\text{DM}}{4\text{-}H_2C{=}\overset{H_3C}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H\overset{H_3C}{\overset{|}{C}}{-}C_6H_4{-}O{-}C_6H_4{-}\overset{CH_3}{\overset{|}{C}}H{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2\text{-}4}$$

Thermal transformations of DM were studied by IR spectroscopy, differential scanning calorimetry (DSC), and elemental, thermogravimetric, and thermomechanical analyses. The IR study of DM was perfoirmed in the temperature range 140–370°C (isothermal heating at 140°C and dynamic heating of a thin film between KBr and NaCl plates at an average rate of 1.4 deg h^{-1}.

The IR spectrum of DM (Fig. 1a, curve *1*) contains absorption bands of unsaturated and aromatic groups at 3070–3060, 3030, 2975, 1630, 1600, 1500, 940, 870, and 830 cm^{-1}, of methyl and methylene groups at 2975, 2930, and 2870 cm^{-1}, and of methine groups at 2900 cm^{-1}; it also contains strong absorption bands of methacrylate ester and diphenyl ether groups at 1715 and 1240 cm^{-1}; bands at 1170, 1060, and

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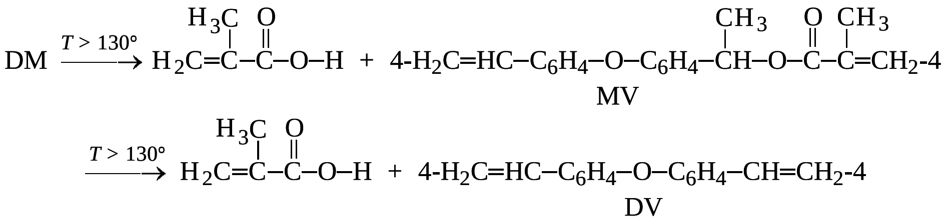
1010 cm^{-1} originate from stretching vibrations of the C–O bond in ester and ether groups.

The mechanism of thermal transformations of another monomer, 4-vinylphenyl-4-(1-methacryloyloxyethyl)phenyl ether (MV), which is also a component of Rolivsan MV-1 [12, 13, 15], has been studied previously [12, 13, 15]. DM can be expected to behave similarly (with corrections for differences in the structure and reactivity), and the following scheme of cleavage (or activation) of latent ester groups with formation of MAA, MV, and bis(4-vinylphenyl) ether (DV) can be suggested:



$$\mathrm{DM} \xrightarrow{T > 130^\circ} \mathrm{H_2C{=}\overset{H_3C}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H} + \text{4-}\underset{\mathrm{MV}}{\mathrm{H_2C{=}HC{-}C_6H_4{-}O{-}C_6H_4{-}\overset{CH_3}{\overset{|}{CH}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2}\text{-4}}$$

$$\xrightarrow{T > 130^\circ} \mathrm{H_2C{=}\overset{H_3C}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H} + \text{4-}\underset{\mathrm{DV}}{\mathrm{H_2C{=}HC{-}C_6H_4{-}O{-}C_6H_4{-}CH{=}CH_2}\text{-4}}$$

It should be noted that, in contrast to MV, even short (1–2 h) heating of DM at 140°C causes substantial changes in the IR spectrum (Fig. 1a, curve *2*), which are due not only to the onset of the expected 3D radical polymerization (the gelation time of DM at 140°C is as short as several minutes) but also to the cleavage of the ester groups, according to the above scheme. Dimethacrylate and bridging units of the initial network polymer, formed by it, are unstable at this temperature and start to noticeably decompose to give MAA and MV, which, in turn, decomposes to DV, MAA, and/or their units. This process gives rise in the IR spectrum of DM to a new band of out-of-plane bending vibrations of the H–C=C fragment of the 4-CH_2=CH–C_6H_4–O–C_6H_4– group at ~902 cm^{-1} [15–18]. The C=C stretching vibration band at 1630 cm^{-1} simultaneously grows in intensity. Therefore, it is not surprising that, in the initial period (1–2 h) of DM heating, the bands at 902 and 1630 cm^{-1} noticeably grow in intensity (Fig. 1a, curve *2*), compared to the starting monomer. However, further heating causes the intiensities of these bands to decrease owing to participation of the methacrylate and styrene groups in (co)polymerization (Fig. 1a, curves *3*–*5*). Therefore, upon prolonged heating of the sample at 140°C and higher temperatures, these bands gradually decrease in intensity, as also does the band at 940 cm^{-1} belonging to out-of-plane bending vibrations of the H–C= fragment of the methacrylate group (Fig. 1a, curves *1*, *2*). Thus, at high temperatures, unsaturated products formed from DM by cleavage of methacrylate groups (see above) are involved in thermal copolymerization of the system, which becomes multicomponent.

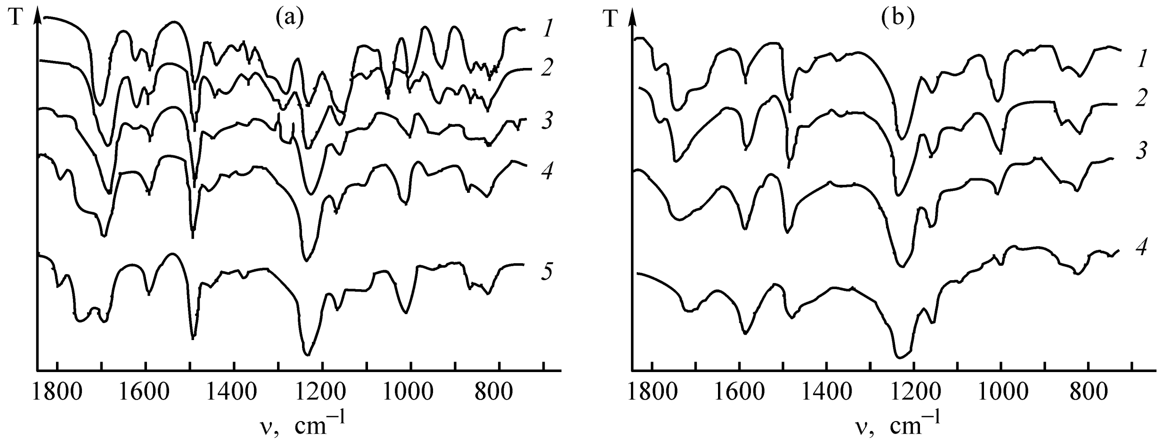


Fig. 1. IR spectra of DM and products of its thermal transformations. Heating rate 1.4 deg h^{-1}. (a) (*1*) Initial DM; heating range 140–190°C; final temperature, °C: (*2*) 142, (*3*) 160, (*4*) 180, and (*5*) 190. (b) Heating range 200–350°C; final temperature, °C: (*1*) 200, (*2*) 260, (*3*) 290, and (*4*) 350. (ν) Wave number and (T) transmission.

Table 1. Conversion of unsaturated and ester groups in the course of dynamic (~1.4 deg h^{-1}) heating of DM, according to IR data*

T, °C	D	c/c_0	D	D	D	c/c_0	D	c/c_0
	at indicated ν, cm^{-1}							
	1630		1240	1060	940		902	
130	0.24	0	0.84	0.60	0.28	0	0.00	0
140	0.20	0.83	0.77	0.05	0.18	0.64	0.11	0.61
150	0.15	0.62	0.83	0.01	0.15	0.54	0.09	0.50
160	0.09	0.38	0.82	–	0.11	0.39	0.05	0.28
170	0.06	0.25	0.85	–	0.06	0.21	0.02	0.11
180	0.04	0.17	0.80	–	0.02	0.07	0.01	0.06

* (D) Optical density; (ν) wave number, cm^{-1}; (c, c_0) running and initial concentrations of functional groups in DM, M. It is assumed that the ratio of the optical densities D/D_0 (D_0, before heating; D, after heating) of DM is proportional to the conversion c/c_0 of the corresponding unsaturated group.

Table 2. Variation of the intensity of some absorption bands in the IR spectra of DM in the course of dynamic (~1.4 deg h^{-1}) heating*

T, °C	D (1803 cm^{-1}), C=O	c_{anhydr}, %	D (1600 cm^{-1}), Ar	D (1500 cm^{-1}), Ar	D (1240 cm^{-1}), O–C in Ar	D (830 cm^{-1}), H–C= in Ar
140/3 h**	0.02	2.0	0.20	0.42	0.77	0.21
140/6 h**	0.03	3.3	0.20	0.44	0.77	0.21
150	0.04	4.4	0.20	0.62	0.87	0.20
160	0.05	5.6	0.19	0.63	0.86	0.20
170	0.07	7.8	0.19	0.50	0.82	0.19
180	0.13	14.4	0.19	0.55	0.80	0.16
190	0.14	15.6	0.20	0.43	0.73	0.16
200	0.15	16.7	0.20	0.42	0.74	0.15
210	0.16	17.8	0.21	0.40	0.78	0.15
220	0.18	20.0	0.22	0.42	0.76	0.16
230	0.17	18.9	0.21	0.37	0.68	0.15
240	0.18	20.0	0.24	0.43	0.76	0.15
250	0.16	17.8	0.24	0.42	0.71	0.14
260	0.14	15.6	0.28	0.41	0.73	0.14
270	0.14	15.6	0.30	0.40	0.77	0.14
280	0.10	11.1	0.31	0.36	0.70	0.14
290	0.08	8.9	0.31	0.30	0.67	0.13
300	0.05	5.6	0.31	0.28	0.61	0.13
310	0.04	4.4	0.33	0.27	0.59	0.12
320	0.04	4.4	0.35	0.26	0.61	0.13
330	0.03	3.3	0.30	0.29	0.64	0.12
340	0.03	3.3	0.34	0.21	0.56	0.10
350	0.01	1.1	0.28	0.17	0.46	0.09
370	0.00	0.0	0.25	0.19	0.38	0.11

* (D) Optical density; 1803 cm^{-1} is the C=O vibration frequency of methacrylic anhydride; Ar = 4-C_6H_4–O–C_6H_4-4; (c_{anhydr}) content of anhydride groups.

** Isothermal heating at 140°C.

Comparison of the IR spectra of DM, MV, and DV monomers (Tables 1, 2) with those of DM thermal transformation products, measured under similar conditions, shows how the degree of DM unsaturation varies in the course of slow dynamic heating in the range 130–180°C. For this purpose, we first determined the experimental intensities of the absorption bands (at 900, 940, and 1630 cm^{-1}) of DM, MV, and

DV monomers used as reference; the IR spectra were recorded under similar conditions.

Let us denote as *A* and *B* the contributions from methacrylate and styrene (4-CH_2=CH–C_5H_4–) groups to the total intensity of an absorption band of the monomer and assume these contributions to be additive. Then the spectrum of DM corresponds to 2*A*; that of MV, to *A* + *B*; and that of DV, to 2*B*. From the spectra of these three monomers, we can estimate that contribution *A* to the bands at 1630, 940, and 900 cm^{-1} is 0.12–0.13, 0.14–0.18, and 0.00, and contribution *B* to the same bands, 0.10–0.11, 0.00, and 0.14–0.18, respectively.

From these data, we can determine how the conversion c/c_0 of the CH_2=CH and CH_2=C(CH_3) groups varies in the course of DM heating. Table 1 shows that, in the range 160–180°C, the concentration of unsaturated groups of the styrene and methacrylate types in the system abruptly decreases owing to their involvement in the radical copolymerization of the system components. It should be noted that the kinetic data obtained in the isothermal (Fig. 2) and dynamic modes of DM heating are well consistent.

As for other major IR manifestations of the cleavage of ester groups in DM, Fig. 1 shows that, on heating, the methacrylate C=O absorption band at 1715 cm^{-1} gets broadened and shifted toward lower frequencies (1700–1685 cm^{-1}) corresponding to absorption of the carboxy group in MAA [15, 18]. Finally, the intensity of the methacrylate C–O stretching band at 1060 cm^{-1} abruptly decreases already at the very beginning of DM heating at 140°C. Simultaneously, the methacrylate H–C= bending band at 940 cm^{-1} gets considerably broadened and shifted owing to superposition of the carboxyl O–H bending band of MAA and/or its unit at 935 ± 15 cm^{-1}; also, broad OH stretching bands of carboxy group appear at 3570–3500 and 2700–2500 cm^{-1}, and a band of the C–O bond in carboxy group appears at 1420 cm^{-1} [19].

It could be expected that cleavage of DM according to the above scheme would be accompanied by a decrease in the content of CH_3 and CH_{tert} groups. Indeed, the intensities of the stretching vibration bands of the methyl (2980, 2930, 2870 cm^{-1}) and methylene (2890 cm^{-1}) C–H bonds and of the C–H bending vibrations (1370 cm^{-1}) appreciably decrease in the course of DM heating. A similar pattern has been observed previously in thermal transformations of other methacrylates of secondary aromatic alcohols [12, 13, 15, 18], e.g., MV [15]. In particular, it was shown that MV units in the network (co)polymer prepared by thermal polymerization of MV are also cleaved to give DV units.

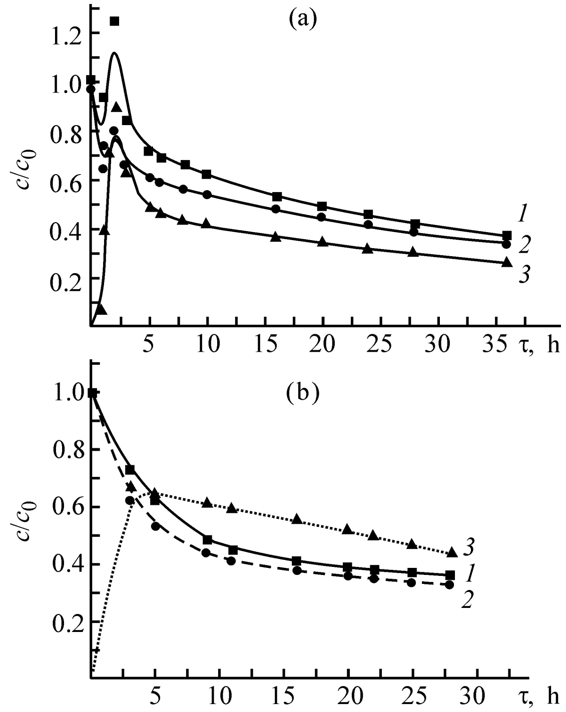


Fig. 2. Kinetics of transformations of unsaturated groups in the course of isothermal heating of DM (140°C) between (a) KBr and (b) NaCl plates. (c, c_0) Initial and running concentrations of functional groups, M. ν, cm^{-1}: (*1*) 1630 [CH_2=CH and CH_2=C(CH_3)], (*2*) 940 [CH_2=C(CH_3)], and (*3*) 902 (CH_2=CH). The c/c_0 ratios were calculated from changes in the intensities of the indicated absorption bands in the IR spectra of transformation products of DM and model monomers (MV, DV).

As the temperature is raised further to 180–200°C and more, one more parallel reaction starts to make a major contribution to the thermal transformations: formation of methacrylic anhydride (MA) units from MAA units in the network polymer, which yields substituted glutaric anhydride units. In the IR spectra of DM recorded in the course of curing, the carbonyl absorption bands at 1803 and 1755 cm^{-1}, characteristic of the anhydride group, steadily grow in intensity (Fig. 1a, curves *4*, *5*; Fig. 1b, curves *1*, *2*; Fig. 3; Table 2). To compare, glutaric anhydride shows carbonyl absorption at 1802 and 1761 cm^{-1} [19]. Naturally, as anhydride units are formed, the absorption band of carboxyl C=O group at 1690 cm^{-1} decreases in intensity.

Heating to 250–300°C causes give rise to broad bands at 1660–1680 cm^{-1} in the IR spectra of DM curing products (Fig. 1b); these bands originate from stretching vibrations of ketone carbonyl group [19].

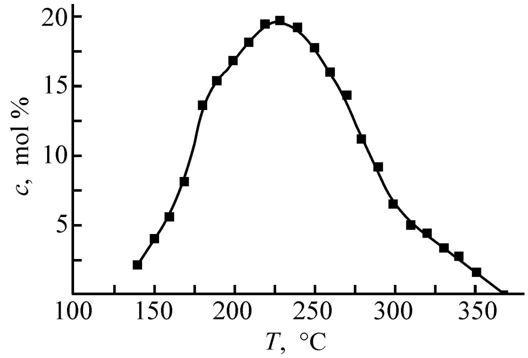


Fig. 3. Kinetics of formation of methacrylic anhydride units in the course of DM heating in the temperature range 140–370°C at average rate of ~1.4 deg min^{-1} between KBr plates: (c) concentration of anhydride groups and (T) temperature.

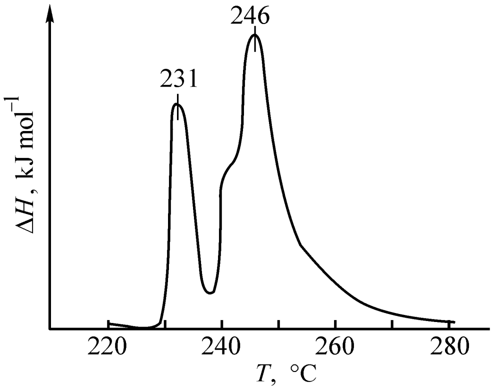


Fig. 4. Thermogram of DM curing (DSC, scanning rate 4 deg min^{-1}). (T) Temperature and (ΔH) thermal effect.

As shown previously in comprehensive studies of related compounds and systems by various methods [12, 13, 15, 18], these changes in the IR spectra are due to fast solid-phase Friedel–Crafts acylation of diphenyl ether groups with adjacent MA units, yielding thermally stable methylenetetralone units in the network copolymer. Figure 3 shows that the consumption of anhydride groups in polymer-analogous acylation reactions results in a fairly sharp decrease in their content in the network copolymer in the final stage of DM curing (in the temperature range 250–300°C).

The IR spectra of products of DM curing in the range 300–370°C allow evaluation of the resistance of units and some groups of the resulting network copolymer to thermal oxidative degradation in air. Figures 1b (curve *4*) and 3 show that the least thermally stable fragments of the copolymer are MA units; they degrade in the course of slow heating of the sample from 300 to 370°C. The intensities of the absorption bands of aromatic and diphenyl ether groups also gradually decrease in the course of prolonged heating, but remain relatively high even after heating to 370°C (Table 2). An exception is an appreciable growth of the band at 1600 cm^{-1}, belonging to the C=C bond in Ar and sensitive to conjugation [19]; apparently, high-temperature degradation results in the formation of polyconjugated (polycyclic) structures.

High-temperature curing of DM and related compounds [15, 18], causing cardinal structural changes as indicated by IR spectroscopy, was also studied by DSC. The observed pattern of thermal effects is consistent with the above-considered mechanism of thermal transformations of DM following from IR data, taking into account a significant difference in the heating rates (IR, 1.4 deg h^{-1}; DSC, 4 deg min^{-1}). At high heating rates, structural changes are usually manifested much more sharply than under conditions of isothermal heat treatment or slow heating.

Figure 4 shows that the exothermic peak observed at 231°C (first step of thermal transformations of DM) is apparently due to prevailing 3D (co)polymerization of methacrylate and styrene monomers. Such processes are accompanied by substantial heat release [20]. In the range 234–238°C, the heat release abruptly weakens, which may be due to prevalent contribution of concomitant endothermic cleavage of ester groups. Finally, the exothermic peaks observed at 240 and 246°C may be due to the major contribution from copolymerization of unsaturated compounds formed by DM cleavage (as shown above) and from polycyclization (formation of anhydride units from MAA units) in the final stage of DM curing (post-curing). The total thermal effect of DM transformations is about 69 kJ mol^{-1}, whereas the heat of polymerization of DV (which contains no cleavable ester groups), determined under the same conditions (kJ mol^{-1}), is considerably higher: 97 [21] or 114 [16]. Thus, the difference in the total heats of curing of DM and DV is mainly due to the fact that curing of DV involves only exothermic reactions of 3D polymerization, whereas curing of DM is accompanied, along with polymerization, by endothermic cleavage of ester groups.

The structural transformations of DM can be generally regarded as high-temperature dehydration, with water removal from the glassy polymeric matrix by molecular diffusion. Presumably, total cleavage of 1 mol of DM or its polymer (polyDM) by the above-given scheme is accompanied by release of 2 mol of MAA (or polyMAA); its transformation into the anhydride, in turn, results in release of 1 mol of H_2O:

$$\underset{\text{PolyDM}}{(C_{24}H_{26}O)_n} \xrightarrow[-H_2O]{160\text{–}230°C} \underset{\text{DV–MA copolymer}}{-(C_{16}H_{14}O)_{n-m}-(C_8H_{10}O_3)_m-},$$

where $n = 1$, $m = 0.5$.

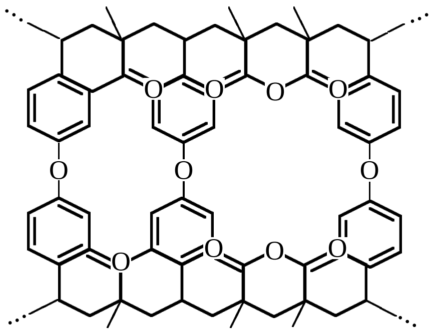
In this case, the molar ratio of DV and MA units in the copolymer will be 1 : 1. Then, if we assume that the high-temperature Friedel–Crafts acylation of diphenyl ether groups with adjacent anhydride groups in polymer chains to give methylenetetralone and MAA units goes to completion, then the composition of the acylated copolymer can be determined from the following scheme:

$$\underset{\text{DV–MA copolymer}}{-(C_{16}H_{14}O)_{0.5}-(C_8H_{10}O_3)_{0.5}-}$$

$$\xrightarrow[-0.25H_2O]{\text{Acylation with MA}} \underset{\text{Acylated DV–MA copolymer}}{-(C_{20}H_{18}O_2)_{0.5}-(C_8H_{10}O_3)_{0.25}-}$$

Elemental analysis shows that, upon heating of DM samples to 300°C, the carbon content grows from 73.2 to 77.7%. The latter value is intermediate between the values calculated for the copolymer compositions before (76.6% C) and after (78.5% C) acylation. Calculation shows that, in the course of formation of these copolymers, transformation of carboxy groups into anhydride groups (followed in the latter case by acylation) should result in the release of 9.6 and 12.1% H_2O, respectively. However, the total amount of volatiles released in the course of dynamic (1.4 deg h^{-1}) heating of DM from 20 to 300°C does not exceed 7.7%. The fact that the amount of released water is lower than expected may be due to partial degradation (decarboxylation) of MAA and anhydride units upon prolonged heating of the samples (for more than 70 h) in the range 200–300°C. Previous mass-spectrometric studies have shown [12, 18] that, at temperatures exceeding 200°C, thermal degradation (mainyl decarboxylation) of methacrylic acid units makes a small but appreciable contribution.

Based on the above data, the polymeric structure finally formed in the course of DM curing at 250–300°C can be represented as follows:



Fast solid-phase reactions in thickly cross-linked polymeric matrices have been studied previously as applied to curing of Rolivsans [5, 6, 21], model systems [12, 13, 18], and related compounds [15, 21]. As noted above, the fact that the reactions occur in thickly cross-linked polymeric matrices at temperatures much lower than the softening point (~403°C), when the transport of reactants to the reaction zone is usually hindered, is an advantage of such systems. However, in the systems under consideration, the vibrational and rotational motion of adjacent groups is sufficiently free for the reactions to be fast [12].

The above-discussed mechanism of DM curing explains why it is possible to prepare heat-resistant polymers and plastics from this thermally unstable monomer. According to dynamic (4.5 deg min^{-1}) thermogravimetric analysis in air, the temperatures of 5 and 10% weight loss by thermally rearranged polyDM are 340 and 390°C, respectively, and the breaking bending stress of fiber glasses based on polyDM is 330 (20°C), 220 (300°C), and 50 MPa (320°C).

EXPERIMENTAL

DM was prepared according to [12, 13]; a colorless glycerol-like liquid, yield 45–50%, n_D^{20} 1.541. Found, %: C 73.20, H 6.6. Ester number (mg KOH per gram product): found 272.0; calculated 274.8.

Bis(4-vinylphenyl) ether (DV) and 4-vinylphenyl 4-(1-methacryloyloxyethyl)phenyl ether (MV) were prepared as described in [12–14].

The IR spectra were measured on a Specord 75-IR spectrometer in a thin film. Calorimetric measurements were performed with a Perkin–Elmer DSC-1B differential scanning microcalorimeter, as described in [20]. Exclusion liquid chromatography (ELC) was carried out on a GPC-Waters chromatograph at 20°C using columns packed with Ultrastyragel 500 Å and $CHCl_3$ or toluene as eluent. Dynamic thermogravimetric analysis of samples was performed on a Paulik–Paulik–Erdey MOM C derivatograph (Hungary) at a heating rate of 4.5 deg min^{-1}. The softening point was determined with a Vicat device (Institute of Macromolecular Compounds, Russian Academy of Sciences; indenter load 1 kg, indenter cross section 1 mm^2).

Fiber glasses were prepared by hot pressing of prepregs on T-10-80 fiber glass fabric at a pressure of ~1 kg cm^{-2}, with heating from 20 to 300°C at a rate of 1.4 deg min^{-1}.

CONCLUSIONS

(1) Thermal transformations of DM yield heat-resistant thermoreactive polymers; common 3D radical polymerization of DM, giving the initial thermally unstable network polymer, is accompanied by thermally initiated solid-phase consecutive-parallel reactions between adjacent groups in chains of the polymer network.

(2) Thermal transformations of DM involve a set of consecutive-parallel reactions of 3D polymerization, cleavage of ester groups of the monomeric unit in the network polymer, formation of anhydride from adjacent MAA units, acylation of diphenyl ether groups with adjacent anhydride groups, decarboxylation of MAA, and degradation of methacrylic anhydride units.

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