J. Serb. Chem. Soc. 69 (6) 441–453 (2004)
JSCS – 3171

UDC 678.744+547.495.1:543.067
Original scientific paper

Dynamical mechanical analysis of photocrosslinked hyperbranched urethane acrylates

ENIS DŽUNUZOVIĆ[1], SRBA TASIĆ[2], BRANISLAV BOŽIĆ[2], DRAGAN BABIĆ[1] and BRANKO DUNJIĆ[2*#]

[1]The "Vinča" Institute of Nuclear Sciences, The Laboratory of Radiation Chemistry and Physics "Gama", P. O. Box 522, 11001 Belgrade and [2]DugaNova Ltd., Viline vode 6, 11000 Belgrade, Serbia and Montenegro

(Received 17 October 2002, revised 17 December 2003)

Abstract: A series of acrylate functionalized samples based on hyperbranched hydroxy-terminated polyesters with different molecular weights and different degrees of acrylation were synthesized. The obtained urethane acrylates were slightly yellow viscose liquids. Their composition was characterized by FTIR and ^{1}H-NMR spectroscopy and their molecular weights were measured by GPC. All the synthesized samples were diluted with 25 wt.% 1,4-butanediol dimethacrylate (BDDM). The rheological properties of the uncured samples and the dynamic mechanical properties of the UV cured samples were examined. All the samples exhibit Newtonian behavior, which indicates the absence of physical entanglements in these polymers. The viscosity increases with increasing number of acrylic groups per molecule. The glass transition temperature of the UV cured samples increases with increasing the number of acrylic groups per molecule. The value of the storage modulus in the rubber-elastic plateau and the cross-link density increase with increasing number of acrylic groups per molecule. The formed networks are inhomogeneous and the residual unsaturation is the highest in the samples with the largest number of acrylic groups per molecule.

Keywords: urethane acrylate, hyperbranched hydroxy-terminated polyester, FTIR, ^{1}H-NMR, GPC, rheology, UV curing, dynamic mechanical properties.

INTRODUCTION

Polymers have traditionally been classified according to their chain architecture into three categories: linear, cross-linked and branched molecules. Recent developments in the synthesis of highly branched systems have led to the inclusion into the general classification scheme of a new class of polymers that mimic the dendritic branching of trees, appropriately called dendritic macromolecules.[1] The family of dendritic macromolecules is further divided into two subgroups: dendrimers and hyperbranched polymers (HBP).[2,3] Dendrimers are well-defined, fully branched,

---

[*] Author for corespondence.

[#] Serbian Chemical Society active member.

monodisperse polymers. Their molecules have a three-dimensional, globular shape, built up of AB_x-functional monomers attached to a B_y-functional core (Fig. 1a). Each repeating unit layer is referred to as a generation.

Dendrimers are ideal in the sense that all repeating units in the inner layers are fully reacted, *i.e.* the degree of branching is equal to unity. The degree of branching (DB) is defined according to Hawker *et al.*[4] as:

$$DB = \frac{\sum\limits_{term} + \sum\limits_{dendritic}}{\sum\limits_{term} + \sum\limits_{dendritic} + \sum\limits_{linear}} \tag{1}$$

where 'term', 'dendritic' and 'linear' refer to terminal groups, dendritic groups and linear groups, respectively. A hyperbranched macromolecule resembles a dendrimer except that the same AB_x monomers are linearly incorporated, leaving B groups unreacted in the interior layers (Fig. 1b). Dendrimers are produced *via* successive protection/deprotection procedures which are often difficult, and expensive. Hyperbranched polymers, on the other hand, can be synthesized by "one-pot" reactions of AB_x-type monomers, making them more interesting for commercial applications.

Hyperbranched polymers are polydisperse and not fully branched, but they may be a suitable alternative because the synthesis is less complex and less time-consuming and the properties of hyperbranched polymers are believed to be similar to those of dendrimers.[5]

Dendritic macromolecules exhibit properties different from those of their linear counterparts, *e.g.*, the melt viscosity for a hyperbranched molecule is considerably lower than that of a corresponding linear polymer of the same molar mass.[6] It has been shown that dendritic polymers exhibit Newtonian behaviour,[6,7] which suggests that no entanglements are formed. These results also indicate that the melt behaviour is mainly determined by surface interactions. The thermal behaviour of hyperbranched polymers is less well understood. Kim and Webster[2] proposed that the glass transition of dendritic polymers has its origin in translation motion and should be more sensitive to the nature of the terminal units and less to molar mass.

Dendritic polymers contain a large number of terminal groups. Their properties are to a large extent dependent on the polarity and the structure of the terminal groups. The physical and/or chemical properties of dendritic polymers can be modified by chemical modification of the terminal groups.[8–11]

Dendritic polymers were considered as suitable for any application where a low viscosity and a large number of functional groups are advantageous. Dendrimers are used as carriers for metal ions,[13] as drug carrier molecules or in gene delivery in medicine, as standards or models for biomolecules or as catalytically active molecules, as thin films with electrical or sensoric properties.[14,15]

Hyperbranched polymers draw much attention as melt modifiers, additives,[2] or blend components[16–19] and coating components.[20–22]

Acrylate functional hyperbranched polyester resins as radiation curable coatings and powder coatings have been investigated by Hult *et al.*.[23–25] The properties of un-

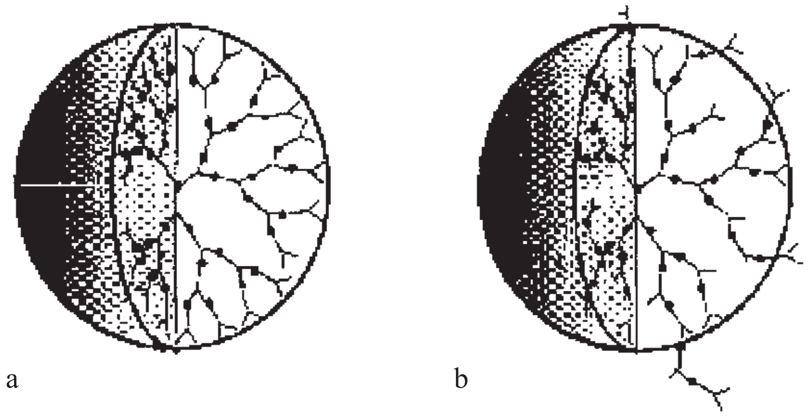

Fig. 1. The structures of dendrimer (a) and hyperbranched molecule (b).[12]

cured and cured resin depend on the type of the end groups and on the degree of acrylation. Variations of the end groups and functionality can be used to tailor a resin for a certain application.

Culbertson *et al.* showed that hyperbranched multi-methacrylate-modified dental resins have acceptable biocompatibility, lower polymerisation shrinkage and improved mechanical properties compared to the commercially used dental resins.[26,27]

One of the most used type of resin in radiation curable coatings are urethane acrylates. Today, the commercially used urethane acrylate resins have linear or slightly branched molecules. Until now, no urethane acrylate resins with a hyperbranched core have been reported. This paper describes the synthesis of urethane acrylates based on hyperbranched hydroxy-terminated polyesters. Two groups of urethane acrylates based on different generation hyperbranched hydroxy-terminated polyesters and with different degrees of acrylation were synthesized. The chemical and rheological properties of the uncured and the mechanical properties of the UV cured urethane acrylates are described. UV cured urethane acrylates were investigated using a torsional dynamic mechanical analyser. All samples of urethane acrylates were diluted with 25 wt.% 1,4-butanediol dimethacrylate (BDDM).

EXPERIMENTAL

Reagents

Di-trimethylolpropane and 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) were obtained from Perstorp AB. Isononanoic acid (3,5,5-trimethylhexanoic acid), from Hoechst, 4-*tert*-butylbenzoic acid, from Aldrich, isophoronediisocyanate (IPDI), from Degussa, 2-hydroxyethyl acrylate (HEA), from Aldrich, 1,4-butanediol dimethacrylate (BDDM), from Bisomer, Irgacure 184 from Ciba-Geigy, dibutyltindilaurate (DBTDL), from Fluka, Desmorapid PP, from Bayer, were used as received without further purification. Chloroform and *n*-pentane were obtained from Merck and used as received.

Synthesis

Synthesis of hyperbranched hydroxy-terminated polyesters. Hyperbranched hydroxy-terminated polyesters (HBP) of the second and the third generation, based on 2,2-bis(hydroxymethyl)propionic acid as the AB_2 monomer and di-trimethylolpropane as the core, were synthesized. Details of the synthesis of the HBP are given elsewhere.[3]

^{13}C-NMR ($CDCl_3$): δ (ppm) 174 (–COO–, bis-MPA), 64.9 (–$\mathit{C}H_2$–OCO–, bis-MPA), 46.5, 48.5, 50.5 (–$(CH_2)_2$–*C*–COO, bis-MPA), 17.6 (–CH_3, bis-MPA).

^{1}H-NMR ($CDCl_3$): δ (ppm) 4.0 – 4.4 (–$C\mathit{H_2}$–OCO–, bis-MPA), 3.6–3.8 (–$C\mathit{H_2}$–OH, bis-MPA), 1.0–1.3 (–CH_3, bis-MPA).

Modification of HBP with isononanoic and p-tert-*butylbenzoic acid*. The modification of 75 % OH groups of HBP was achieved *via* esterification with isononanoic (IA) and 4-*tert*-butylbenzoic acid (*pt*BBA). The synthesis of HBP4 is described as an example. HBP2 (79.27 g, 0.0226 mol) was placed in a four-necked flask, equipped with a mechanical stirrer, a Dean-Stark apparatus, a thermometer and a nitrogen inlet, and melted at 140 ºC. Then isononic acid (66.45 g, 0.420 mol) and *p-tert*-butylbenzoic acid (24.20 g, 0.136 mol) were added and the mixture was heated to 170 ºC. Xylol (6 ml) was added and the reaction mixture was kept at 200–220 ºC for 13 h, after which time, vacuum was applied for 1 h before the reaction mixture was removed from the flask.

^{13}C-NMR ($CDCl_3$): δ (ppm) 172.5 (–CO–, bis-MPA), 171.8 ($(CH_3)_3CCH_2CH(CH_3)CH_2$–*CO*–), 166.0 (–CO–, *pt*-BBA), 157.0, 129.5, 127.1, 125.4 (C_{Ar}, *pt*-BBA), 64.9 (–CH_2–, bis-MPA), 50.5 ($(CH_3)_3C\mathit{C}H_2CH(CH_3)CH_2$–CO–), 48.8, 46.5 (–$(CH_2)_2$–*C*–COO, bis-MPA), 43.5 ($(CH_3)_3CCH_2CH(CH_3)\mathit{C}H_2$–CO–), 35.0 ($(CH_3)_3$–*C*–Ar, *pt*-BBA), 31.0 ($(\mathit{C}H_3)_3$–C–Ar, *pt*-BBA), 29.8 ($(\mathit{C}H_3)_3CCH_2CH(CH_3)CH_2$–CO–), 26.0 ($(CH_3)_3\mathit{C}CH_2CH(CH_3)CH_2$–CO–), 22.5 ($(CH_3)_3CCH_2\mathit{C}H(\mathit{C}H_3)CH_2$–CO–), 17.6 ($CH_3$–, bis-MPA).

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.9, 7.45 (H-Ar, *pt*-BBA), 4.0–4.45 (–CH_2–OCO–, bis-MPA), 3.6–3.7 (–$C\mathit{H_2}$–OH, bis-MPA), 2.2–2.3 ($(CH_3)_3CCH_2C\mathit{H}(CH_3)CH_2$–CO–), 2.15 ($(CH_3)_3CCH_2CH(CH_3)\,C\mathit{H_2}$–CO–).

Synthesis of hyperbranched urethane acrylates. All samples of hyperbranched urethane acrylates (HBUA), with a different number of acrylate groups as terminal units, were synthesized according to the same general procedure as described for HBUA3-4 below. The urethane acrylates were synthesized in two steps: firstly synthesis of the adduct with NCO and acrylic groups from IPDI and HEA and secondly modifcation of the 75 % modified hyperbranched polyesters (previously described) with the synthesized adduct.

Synthesis of NCO-bearing adduct. IPDI (59.14 g, 0.266 mol), hydroquinone (0.119 g) and DBTDL (0.236 g) were added to a three-necked flask equipped with a magnetic stirrer, a dropping funnel with a water condenser capped with a drying tube, a thermometer and a nitrogen inlet tube. The flask was placed in an oil bath previously heated to 50 ºC. HEA (30.86 g, 0.266 mol) was added dropwise over 2 h to the stirred reaction mixture. Stirring was continued until the absorption peak of the OH group in the infrared spectra had disappeared. The reaction mixture was not purified. All the reaction mixtures, slightly yellow viscous liquid, were used as an adduct. FTIR (cm^{-1}): 2267 (NCO), 1734 (ester carbonyl), 3360 (NH), 1638 and 812 (acrylate unsaturation).

Modification of the hyperbranched hydroxy-terminated polymers with the synthesized adduct. Modification of hyperbranched hydroxy-terminated polymers with the synthesized adduct is exemplified by the synthesis of HBUA3-4, HBP4 (25.14 g, 0.0253 mol OH), DBTDL (0.06 g), hydroquinone (0.02 g), Desmorapid PP (0.07 g) and BDDM (3.22 g) were added to a four-necked flask equipped with a mechanical stirrer, a dropping funnel with a water condenser capped with a drying tube, a thermometer and a nitrogen inlet tube. The flask was placed in an oil bath previously heated to 80 ºC. The adduct (3.66 g) was mixed with BDDM (2.45 g) and the mixture was added dropwise to the flask under stirring. The reaction was followed by IR spectroscopy. After nine hours, the absorption peak of the NCO groups at 2267 cm^{-1} had disappeared and the reaction was stopped. The reaction mixture was not purified. BDDM (4.03 g) was added to the mixture, up to 25 wt.% of the reaction mixture.

FTIR (cm^{-1}): 1638 and 812 (acrylate unsaturation), 1734 (ester carbonyl), 3360 (NH). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.35 – 6.45 (*d*, 1H, *cis*, –$CH{=}CH_2$), 6.03–6.18 (*m*, 1H, –$CH{=}CH_2$), 5.78–5.85 (*d*, 1H, *trans*, –$CH{=}CH_2$). GPC: $M_n = 3733$ g mol^{-1}, $M_w = 9794$ g mol^{-1}, $M_w/M_n = 2.62$.

Sample preparation

As the syntheses were performed in BDDM, the pure HBUA were isolated by precipitation in *n*-pentane. These precipitated samples were used for FT-IR and NMR measurements.

Photocrosslinkable systems were obtained by mixing urethane acrylate, 4 wt.% Irgacure 184 (photoinitiator) and 25 wt.% BDDM as reactive diluents.

A portable 2 curing system (UVPS, Inc) with a medium pressure mercury lamp (80 W/cm) was used as the ultraviolet irradiation source.

The samples for dynamic mechanical measurements (63×12×1 mm) were cured in sandwiches between two thin polyester foils. The samples were irradiated from both sides at a distance of 10 cm from the lamp for 20 min.

Characterization

FTIR and NMR characteristics. The composition of synthesized samples were determined by ^{1}H-NMR and ^{13}C-NMR (Varian-Gemini 200 MHz) using solution in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. The characteristic absorption peaks of the functional groups were detected during the synthesis reactions using a Bomem MB-102 Fourier transform infrared (FT-IR) spectrometer.

GPC Measurement of molecular weight. The molecular weight and molecular weight distributions of the urethane acrylates were measured using a Varian 9010 GPC equipped with a refractive index detector and five TSK-GEL H columns (from Tosoh Corporation). Tetrahydrofuran, 1.0 ml min^{-1} was used as the mobile phase. Calibration was carried out using linear polystyrene samples of known molecular weight and dispersity.

Dynamic mechanical measurements. The complex dynamic viscosity (η*) of the urethane acrylate with 25 wt.% BDDM were recorded using a Rheometrics mechanical spectrometer RMS-605 operating in the rate sweep mode, using a cone and plate geometry at 25 ºC. The frequency range was 0.1–100 rad s^{-1}, and the strain was fixed at 30 %.

The dynamical torsion tests of the UV cured samples (63×12×1 mm) were performed using the same instrument, a Rheometrics RMS-605, in the temperature sweep mode. The examinations were carried out between 20º and 220 ºC at 6.28 rad s^{-1} at a fixed strain of 0.25 %.

RESULTS AND DISCUSSION

Synthesis and chemical characterization

The properties of the synthesized hyperbranched hydroxy-terminated polyesters of the second and the third generation are shown in Table I. The content of each building unit was determined using ^{13}C-NMR spectroscopy.[4] The degree of branching (DB) was calculated from Eq. (1) and determined to be 0.44 for both samples. The DB seems to be independent of the stoichiometric ratio between the core molecule and the repeating unit.

TABLE I. The properties of the used hyperbranched polyesters

HBP	Generation	OH/molecule (Theor.)	OH value (Theor.) mg KOH/g	OH value (Exp.) mg KOH/g	$M_{theor.}$ g/mol	DB (NMR)
HBP1	2	16	66.3	61.8	1642	0.44
HBP2	3	32	64.3	56.4	3498	0.44

The samples HBP1 and HBP2 were modified with isononanoic and *p-tert*-butylbenzoic acid. The composition of the obtained modified HBP (HBP3 and HBP4) was determined using ^{1}H-NMR spectroscopy. The results are shown in Table II.

TABLE II. The composition of the partially modified HBP

HBP	Generation	M_{theor}, g/mol	OH/molecule	IA/molecule	*pt*-BBA/molecule
HBP3	2	3382	4	9	3
HBP4	3	6980	8	18	6

The urethane acrylates were synthesized from the adduct and partially modified hyperbranched hydroxy-terminated polyesters. The reaction route for the preparation of the adduct from HEA and IPDI is shown schematically in Fig. 2. The urethane linkages were obtained from the reaction of the OH groups from HEA with the NCO groups from IPDI. In the FTIR spectra, the absorption peak of OH groups disappeared and a new absorption peak of the NH groups appeared, which confirmed the structure of the adduct.

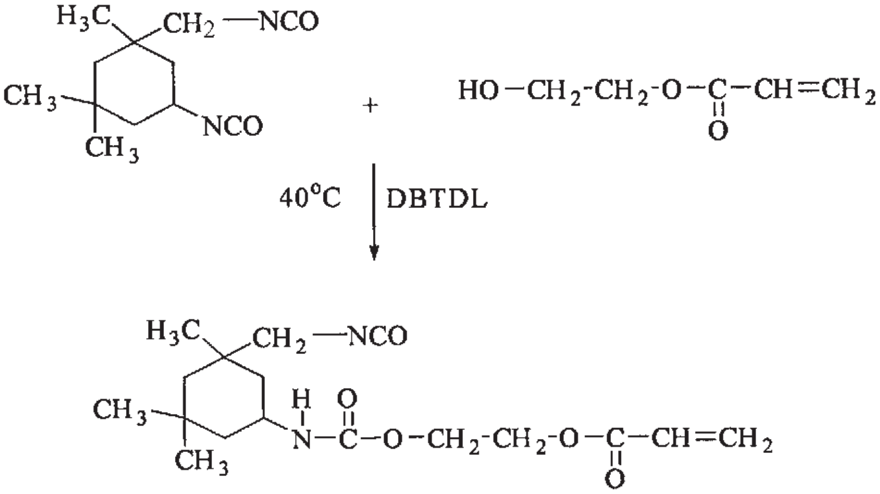

Fig. 2. Schematic representation of the synthesis of the adduct.

An idealized reaction scheme for the synthesis of the urethane acrylates from the adduct and the partially modified hyperbranched hydroxy-terminated polyesters is presented in Fig. 3. The synthesis of HBUA was performed in BDDM which served as a reactive diluent in the photo crosslinkable composition. By using BDDM as a solvent, the viscosity of the reaction mixture was reduced and the product was ready for use without any additional treatment. Both the FTIR and NMR spectra (Fig. 4) confirmed the structures of synthesized urethane acrylates. An attempt was made to obtain a pure sample by multiple precipitations in *n*-pentane. However, some amount of BDDM remained, which can be seen in the ^{1}H-NMR spectrum. The peaks of methacrylic group are at 6.1 and 5.48 (CH_2) and 1.9 (CH_3). The results of the characterization of HBUA are given in Table III. The number of acrylic groups per molecule of urethane acrylates was calculated from the ^{1}H-NMR spectra as follows:

$$N_{\text{arom/molHBP}} = \frac{I_{(7.38-7.95)}}{I_{3.29}} \tag{2}$$

$$N_{\text{C=C/molHBP}} = \frac{4 \times N_{\text{arom/molHBP}} \times (I_{(5.70-6.48)} - I_{5.48})}{3 \times I_{(7.38-7.95)}} \tag{3}$$

where: $I_{(7.38–7.95)}$ – integration of the protons from the aromatic ring; integration of $–CH_2–O–CH_2–$protons(from di-trimethylolpropane in HBP core), $I_{5.48}$ – integration of the proton from the methacrylic group; $I_{(5.70–6.48)}$ – integration of the protons from the acrylic and methacrylic groups

The number of aromatic rings attached to the hyperbranched core for each generation was estimated using Eq. (2). Then, by comparing the intensities of the acrylic protons to the aromatic ones, the number of C=C groups per HB core molecule was estimated.

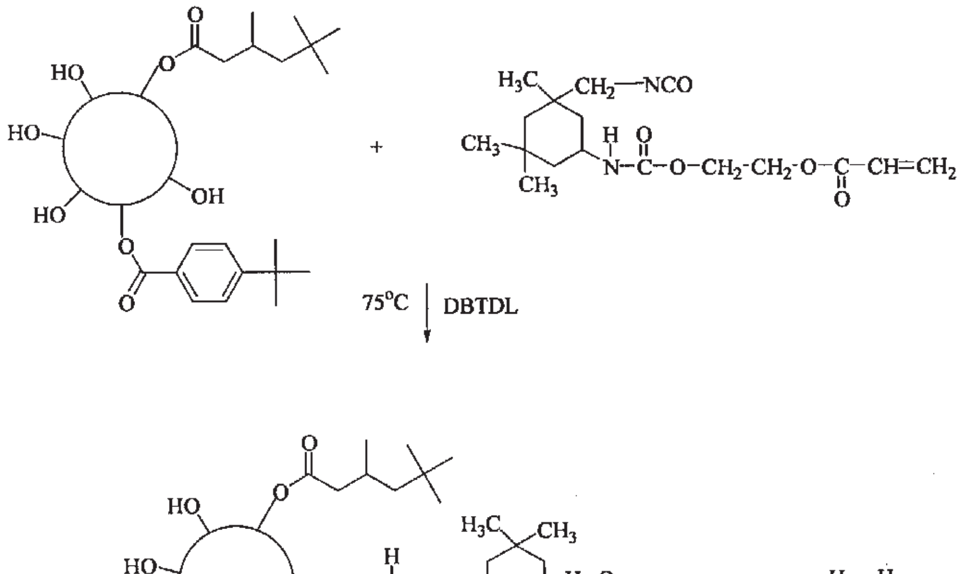

Fig. 3. Schematic representation of the synthesis of HBUA.

Comparing the NMR spectra of the urethane acrylates with the NMR spectra of the corresponding unmodified hyperbranched hydroxy-terminated polymer, the number of acrylic groups per molecule of urethane acrylates was found to be less than theoretical, Table III. The reason for this behaviour is probably the reduced reactivity of the OH groups due to steric hindrance. Before the calculations, the residual amounts of

BDDM were subtracted. The number of acrylic groups per molecule of urethane acrylates was also calculated from the hydroxyl value. The obtained values were different from the values obtained by ^{1}H-NMR spectroscopy.

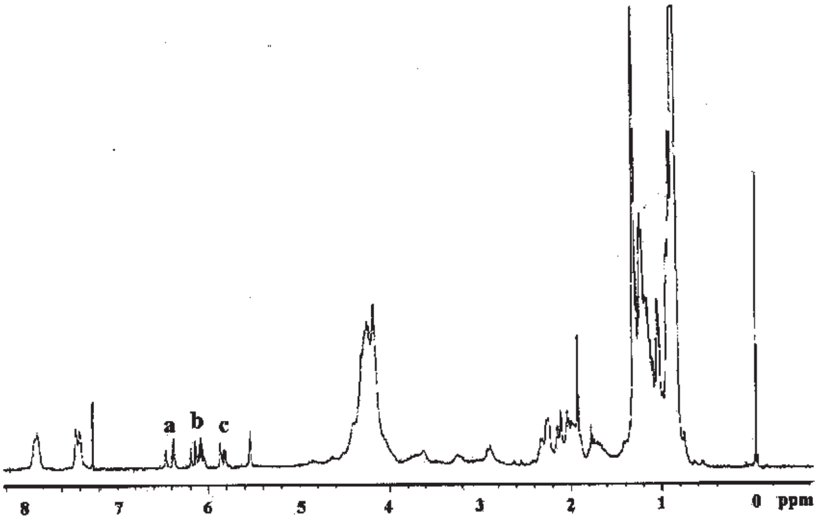

Fig. 4. ^{1}H-NMR of HBUA3-4 in $CDCl_3$.

The molar masses of the dendritic polymers determined by GPC were below the estimated values, due to their highly branched nature.[24] The molecular weight and molecular weight distribution of the samples in this study were analysed by GPC, Table II. The GPC instrument was calibrated with linear polystyrene samples which have a different correlation between hydrodynamic volume and elution time than the analysed hyperbranched polymers. The GPC values of hyperbranched polymers generally give lower molecular weights than they should be, but the GPC values give reasonably accurate information about the polydispersity of the polymers. The GPC values show that the molecular weight differences between the theoretical calculation and GPC measurement increase and the polydispersity index becomes larger with increasing molecular weight. There are two main reasons for the increase of the molecular weight difference between the theoretical value and the GPC value. The first reason is cyclization during the preparation of hyperbrancehd hydroxy-terminated polyesters, which decreases the molecular weight, especially for the higher generation.[26] The second reason is that the hydrodynamic volume of HBP does not increase linearly with increasing molecular weight. The increase of polydispersity index is probably due to the presence of small quantities of unreacted IPDI that can lead to chain extension. The FT-IR spectra of all the synthesized urethane acrylates had peaks at 1638 and 810 cm^{-1}, both corresponding to acrylates.

Rheology of uncured samples

The dependence of the complex dynamic viscosity on frequency is shown in Fig. 5. For all samples, the viscosity was found to be independent of frequency, which

TABLE III. The properties of the synthesized urethane acrylates

Sample	HBUA2-2	HBUA2-3	HBUA2-4	HBUA3-4	HBUA3.6	HBUA3-8
Generation	2	2	2	3	3	3
C=C/molecule (theor.)	2	3	4	4	6	8
C=C/molecule (^{1}H-NMR)	2.38	3.03	3.28	2.80	3.44	5.50
C=C/molecule (OH value)	1.4	3.2	2.6	4.51	–	4.87
M_{theor}, g/mol	4058	4396	4734	8332	9008	9684
M_{n}, g/mol (GPC)	2784	2984	2755	3733	3736	3414
M_{w}, g/mol (GPC)	4530	4674	5344	9794	10773	11880
$M_{\mathrm{w}}/M_{\mathrm{n}}$ (GPC)	1.63	1.57	1.94	2.62	2.88	3.48
η/Pas (75 wt.% in BDDM)	13.9	19.2	32.7	35.6	63.1	70.6

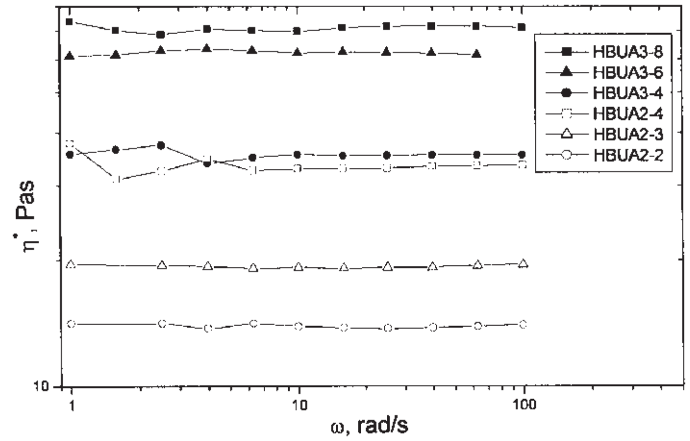

Fig. 5. Complex dynamic viscosity *vs*. frequency at 25 °C of the urethane acrylates with 25 wt.% BDDM.

is characteristic of a Newtonian fluid. It has been proposed that the lack of entanglements in dendritic materials is the cause of their Newtonian features, which have often been reported in the literature to date.[6,28] The samples of urethane acrylates of the third generation have a larger viscosity than the urethane acrylates of the second generation, probably due to their higher molar mass. Comparing the samples based on the same generation it can be seen that the viscosity increases with the degree of acrylation *i.e.*, with the urethane bond concentration. The most likely cause for this behavior is the degree of polar interaction between the urethane linkages and/or OH groups.

Mechanical properties of UV cured samples

All the urethane acrylate samples were UV cured to yield solid products. The curing was performed in sandwiches between two polyester foils which were used in order to provide samples having a proper form and to avoid oxygen inhibition of the curing reaction.

TABLE IV. The properties of the UV cured samples of urethane acrylates determined by DMA analysis

Sample	HBUA2-2	HBUA2-3	HBUA2-4	HBUA3-4	HBUA3-6	HBUA3-8
G'_e/MPa	10.04	14.60	33.85	13.63	16.33	39.75
T_g/°C	53	62	74	45	56	71
Residual unsaturation/%	18.0	16.4	23.7	11.8	16.3	19.0

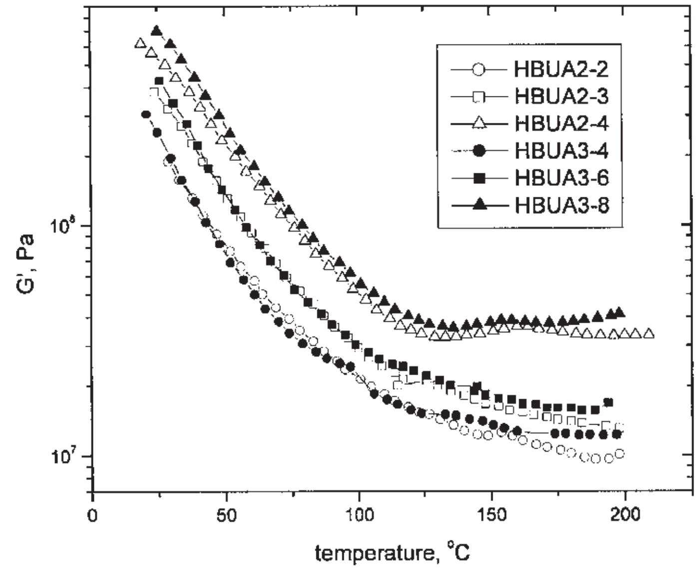

Fig. 6. Storage modulus *vs*. temperature for UV cured samples of urethane acrylates.

Dynamic mechanical measurements were used to determine the change in the mechanical properties of the UV cured samples of urethane acrylates with temperature. The temperature dependence of the storage modulus (G') is shown in Fig. 6. For all samples, a rubber-elastic plateau was observed above 120 °C. Three pairs of curves were obtained, which indicated that G' is independent of the generation of the HBP core. G' is only dependent on the degree of acrylation. G' increases with increasing number of acrylic groups per molecule, which corresponds to an increase in the cross-link density.

The value of glass transition temperature (T_g), obtained as the maximum value of the tan(δ) peak, increases from 45 °C for HBUA3-4 to 74 °C for HBUA2-4 (Fig. 7 and Table IV). This indicates that a higher crosslink density is obtained by increasing the functionality. The T_g increases with increasing number of acrylic groups per molecule of urethane acrylates of the same generation while it does not depend on the HBP core generation. The network homogeneity of the UV cured samples are expressed by the width of the tan(δ) peaks. Broad tan(δ) peaks were obtained for all samples, indicating

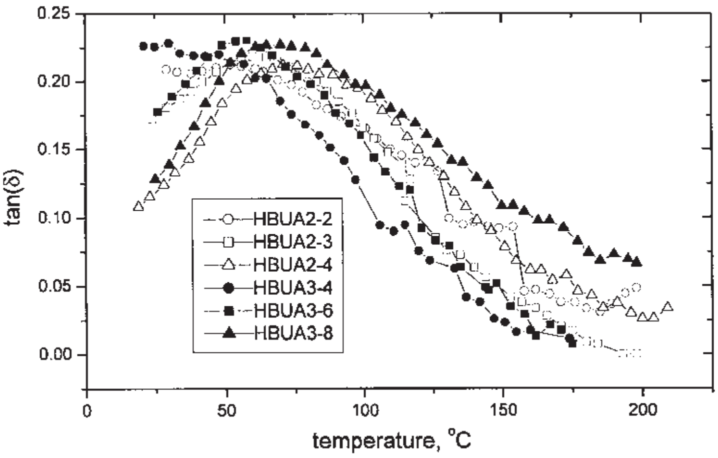

Fig. 7. Tan(δ) *vs*. temperature for UV cured samples of urethane acrylates.

that the formed networks are inhomogeneous.[25]

The residual unsaturation was determined by FTIR spectroscopy. The FTIR spectra of the cured samples compared with the spectra of the uncured ones show that the residual unsaturation is the highest for the samples with the largest number of acrylic groups per molecule for both generations.

CONCLUSIONS

A series of urethane acrylates based on second and third generation hyperbranched hydroxy-terminated polyesters with different degrees of acrylation were synthesized and characterized. All the synthesized urethane acrylates showed characteristics of a Newtonian fluid. The viscosity of these samples increases with increasing molecular weights and degree of acrylation. All samples were UV cured. The mechanical properties of the UV cured samples were less dependent on the molecular weight than on the degree of acrylation. The glass transition temperature of the UV cured samples increases with increasing degree of acrylation. G'_e and the cross-link density increase with increasing degree of acrylation. The formed networks of all samples were inhomogeneous. The residual unsaturation increased with increasing degree of acrylation.

Acknowledgment: We would like to thank Vesna Aleksandrović, M. Sc., for help with the DMA measurements.

ИЗВОД

ДИНАМИЧКО–МЕХАНИЧКА АНАЛИЗА ФОТОУМРЕЖЕНИХ ХИПЕРРАЗГРАНАТИХ УРЕТАН–АКРИЛАТА

ЕНИС ЏУНУЗОВИЋ[1], СРБА ТАСИЋ[2], БРАНИСЛАВ БОЖИЋ[2], ДРАГАН БАБИЋ[1] и БРАНКО ДУЊИЋ[2]

[1]Институт за нуклеарне науке "Винча", Лабораторија за радијациону хемију и физику "Гама", п. пр. 522, 11001 Београд и [2]ДугаНова, Вилине воде 6, 11000 Београд

Синтетисана је серија акрилованих узорака базирана на хиперразгранатим хидрокситерминираним полиестрима са различитим моларним масама и различитим степеном акриловања. Добијени уретан-акрилати су били слабо жуте вискозне течности. Њихов састав одређен је FTIR и ^{1}H-NMR анализом, а моларна маса мерена је методом GPC. Сви синтетисани узорци разблажени су са 25 мас.% 1,4-бутандиолдиметакрилата (BDDM). Испитивана су реолошка својства неумрежених узорака и динамичко–механичка својства узорака умрежених дејством УВ зрачења. Сви узорци су показали њутновско понашање, што указује на одсуство физичког умрежења (преплетаја) у овим полимерима. Вискозност неумрежених узорака расте са повећањем броја акрилних група по молекулу. Температура стакластог прелаза узорака умрежених дејством UV зрачења расте са повећањем броја акрилних група по молекулу. Вредности модула сачуване енергије у платоу гумоликоеластичног стања и густина умрежености расту са повећањем броја акрилних група по молекулу. Настала полимерна мрежа је нехомогена и заостало незасићење је највеће за узорке са највећим бројем акрилних група по молекулу.

(Примљено 17. октобра 2002, ревидирано 17. децембра 2003)

REFERENCES

1. D. A. Tomalia, R. Esfand, *Chem. Ind.* **11** (1997) 416
2. Y. H. Kim, O. W. Webster, *Macromolecules* **25** (1992) 5561
3. E. Malmström, M. Johansson, A. Hult, *Macromolecules* **28** (1995) 1698
4. C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **113** (1991) 4583
5. F. Chu, C. J. Hawker, *Polym. Bull.* **30** (1993) 265
6. C. J. Hawker, P. J. Farrington, M. E. McKay, K. L. Wooley, J. M. J. Fréchet, *J. Am. Chem. Soc.* **117** (1995) 4409
7. A. Hult, M. Johansson, E. Malmström, *Macromol. Symp.* **98** (1995) 1159
8. E. Malmström, A. Hult, U. W. Gedde, F. Liu, R. H. Boyd, *Polymer* **38** (1997) 4873
9. D. Schmaljohann, L. Häußler, P. Pötschke, B. I. Voit, T. J. A. Loontjens, *Macromol. Chem. Phys.* **201** (2000) 49
10. E. Malmström, M. Johansson, A. Hult, *Macromol. Chem. Phys.* **197** (1996) 3199
11. A. Brenner, B. I. Voit, D. J. Massa, S. R. Turner, *Macromol. Symp.* **102** (1996) 47
12. T. Glauser, *Ph. D. Thesis*, Kungliga Tekniska Högskolan, Stockholm, 1999. p. 14
13. G. Bar, S. Rubin, R. W. Cutts, T. N. Taylor, T. A. Zawodrinski, Jr. *Langmuir* **12** (1996) 1172
14. Y. Zhou, M. L. Bruening, D. E. Bergbreiter, R. M. Crooks, M. Wells, *J. Am. Chem. Soc.* **118** (1996) 3773
15. M. Wells, R. M. Crooks, *J. Am. Chem. Soc.* **118** (1996) 3988
16. J. Jang, J. H. Oh, S. I. Moon, *Macromolecules* **33** (2000) 1864
17. C. M. Huner, B.-S. Chiou, A. L. Andrady, S. A. Khan, *Macromolecules* **33** (2000) 1720
18. D. Schmaljohann, P. Pötschke, R. Hässler, B. I. Voit, *Macromolecules* **32** (1999) 6333
19. D. J. Massa, K. A. Shriner, S. R. Turner, B. I. Voit, *Macromolecules* **28** (1995) 3214
20. M. Johansson, E. Malmström, A. Hult, *J. Appl. Polym. Sci.* **31** (1993) 619

21. J. Lange, E. Stenroos, M. Johansson, E. Malmström, *Polymer* **42** (2001) 7403
22. D. Schmaljohann, B. I. Voit, J. F. G. A. Jansen, P. Hendriks, J. A. Loontjens, *Macromol. Mater. Eng.* **257** (2000) 31
23. M. Johansson, E. Malmström, A. Jansson, A. Hult, *J. Coatings Technology* **72** (2000) 906
24. M. Johansson, A. Hult, *J. Coatings Technology* **67** (1995) 35
25. M. Johansson, T. Glauser, G. Rospo, A. Hult, *J. Appl. Polym. Sci.* **75** (2000) 612
26. Q. Wan, S. R. Schricker, B. M. Culbertson, *J. M. S.-Pure Appl. Chem.* **37** (2000) 1301
27. Q. Wan, D. Rumpf, S. R. Schricker, A. Mariotti, B. M. Culbertson, *Biomacromolecules* **2** (2001) 217
28. P. J. Farrington, C. J. Hawker, J. M. J. Fréchet, M. E. Machay, *Macromolecules* **31** (1998) 5043.