

Structure-Property Relations in UV-Curable Urethane Acrylate Oligomers

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ABSTRACT: Four urethane acrylate oligomers were synthesized by a reaction of an excess of isophorone diisocyanate (D) with polypropylene glycol Acclaim 4200N (P) with a subsequent reaction of nonreacted D with a hydroxy acrylate Tone M100 (A). The latter has a common name caprolactone acrylate. Oligomers were prepared by different ways of addition of P to D or D to P and at different ratio of [D]/[P]. The fifth oligomer ADA was prepared as an individual compound. Viscosities, GPC traces, T_g 's of oligomers were taken alongside with other physical properties of cured oligomers. It was demonstrated that oligomers with P con-

sist of ADPDA, ADA, and of a chain-extended product A. . . P_n. . . A, which has two or more Ps in a molecule. Additive contributions of these three components essentially determine properties of the liquid and cured oligomers. Structure-property relations of urethane acrylate oligomers are discussed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 489–494, 2006

Key words: polyurethanes; curing of polymers; oligomers; coatings; gel permeation chromatography

INTRODUCTION

Coatings based on urethane acrylate oligomers (UAOs) are widely used in the industry.^{1–4} Purposeful formulation of coatings with desired properties and study of properties of UAOs are important tasks of applied polymer science. A common UAO is formed by a reaction of diisocyanate (D) with a polyol (P) at an equivalent ratio of approximately two isocyanate groups to one hydroxyl group (D : P = 2 : 1), forming a urethane prepolymer. To have radiation-curable oligomers, urethane prepolymer is blocked with acrylate (A).^{1–5}

It was reported that D and P have an essential effect on properties of liquid and cured coatings.⁴ The common three D were studied: IPDI, H₁₂MDI, and TDI. UAOs were cured in the presence of 30% of reactive diluent.⁴

We have demonstrated that an order of addition of the same reagents in the same amounts at UAO synthesis essentially affects properties of the prepared liquid UAOs.³

In the present work, we continued to study properties of liquid and cured UAOs presented previously.^{3,4} In contrast to the work done by McConnell et al., UAOs were prepared from the same three reagents D,

P, and A by different ways with a goal of understanding structure-properties relation of UAOs. We did not use any reactive diluents during cure in order to get that relation unmasked by an addition of a diluent.

EXPERIMENTAL

Reagents

P was difunctional polypropylene glycol Acclaim 4200N from Bayer, with a hydroxyl number (OH#) 28.0. A was Tone M100 from Dow. The latter has a common name of caprolactone acrylate, and it is an oligomer with an average two-opened ϵ -caprolactone fragments. We used Tone M100 with OH# of 162.1. Isophorone diisocyanate (D) was from Rhodia, a catalyst of urethane synthesis dibutyltin dilaurate (Fascat 4202 from Atofina) was used at a level of 500 ppm on a total mass of a batch. Irganox 1010 (from Ciba Additives) was an inhibitor of spontaneous polymerization, and it was added at 500 ppm level based on a total mass of a batch. All compounds were used as received.

Cure of samples

Photoinitiator Irgacure 4265 of Ciba Specialty Chemicals was dissolved in warm samples in a concentration of 2.0 wt %. Samples were cured with Fusion 300 W/in processor with D-bulb in the air. Two passes under a processor at a conveyor speed of 20 ft/min

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were enough to cure films under our experimental conditions. The completeness of cure was confirmed by a complete disappearance of acrylate group absorption band (812 cm^{-1}) in IR spectra of cured films, cf. below.

The thickness of each cured film was measured with a micrometer, and it was about 0.5 mm.

Devices

Properties of products were analyzed with gel permeation chromatography (GPC), which give molecular weights as weight average and number average (M_w and M_n), and the molecular weight distribution $MWD = M_w/M_n$. GPC device and GPC experiments are described elsewhere.³ All compounds on GPC trace were included in calculation of molecular weights. In particular, a relatively low M_w compound ADA was included into calculation.

The IR spectrometer was Perkin–Elmer Spectrum One model with a diamond crystal UATR.

Viscosity (η) was measured with Brookfield RVT with small adapter (spindle SC4–15 and cup 7R) connected to a Neslab circulating water bath at 25°C.

Tensile properties of cured samples (elongation to break, tensile strength at break, tensile modulus) were measured with Cheminstruments Tensile Tester–1000. The test method was designed to be in compliance with ASTM D 822. A tester was controlled by Cheminstruments EZ-Lab system program. At least five samples of each cured UAO were studied at ambient temperature to verify reproducibility of data.

Dynamic mechanical properties were measured with TA Instruments AR2000 controlled stress rheometer. After measurement of the linear viscoelastic region for each material, strain was selected at 1%. T_g values of cured oligomers were of the main interest. In accordance with a common practice, we identified T_g with $\tan \delta = G''/G'$, where G'' is a shear loss modulus, and G' is a shear storage modulus.

Syntheses

Four oligomers were prepared in a very similar way.³ The reactions were run at 60°C, and the reactants were added in a manner to keep the reaction temperature under 70°C. All syntheses started with D, catalyst, and inhibitor in the pot and the remaining ingredients were added in. In the first stage of a process, P was added to the excess of D. The reaction took place over a period of 2 h. After that, in the second stage, products of the first stage reacted with added A over a period of 8 h. We prepared batches with a ratio of equivalents of P : D : A as 1 : 2 : 1 and with the same ratio of 1 : 6 : 5. We name these oligomers as UAO[2a] and UAO[6], respectively, cf. the Table I.

We prepared UAO, which we named UAO[b] (b stands for “blend”), in one pot using the same total amounts of the same reagents as in the synthesis UAO[6], cf. above. However, we reacted first smaller amounts of D, P, and A to get oligomer UAO[2a]. We added additional amounts of D and A (equivalents D : A = 1 : 1) after that, cf. Table I.

In one stage synthesis, we prepared a relatively low M_w compound ADA by with equivalents D : A = 1 : 1. The synthesis was performed in a similar way like syntheses with P; cf. above. Temperature was kept not higher than 70°C. ADA is an adduct of two As and D, and we named it diadduct or UAO[d], Table I.

The last batch UAO[2b] (Table I) was prepared almost the same way as UAO[2a] with the only difference that in the first stage, D was added to P.

We took IR spectra of reactive mixtures paying particular attention to the peak at 2230 cm^{-1} (NCO), watching for the completeness of reaction via extinction of isocyanate. All performed syntheses were complete by IR (<0.2% absorption of residual NCO). Similarly, IR spectra demonstrated the completeness of cure when we observed <0.2% of initial absorption of acrylate groups (cf. above).

All syntheses were performed in a 1-L flask; the final product had a mass of 700–750 g. A synthesis of each of five batches was repeated two to three times using the same raw materials, to verify reproducibility of data.

RESULTS

The first stage of a process leads to formation of DPD:^{1–3}



Products of chain extension DPDPD, DPDPDPD, . . . are formed in the first stage as well.

ADPDA is made in the second stage:^{1–4}



alongside with endcapped chain-extended products. We abbreviate all chain-extended acrylated products with two and more P in their structures as A . . . P_n . . . A. Low MW product ADA is formed in the second stage also. Evidently, any order of addition of A, P, and D leads to consumption of all OH and NCO groups, because reagents were selected the way that total equivalents of OH equal to the total equivalents of NCO.

Figures 1–3 present GPC traces of the five prepared UAOs. Obtained GPC reports provide percentile fraction of total area related to a peak. We assume that the reported percentile reflects a relative concentration of each fraction. (More accurate estimation of concentra-

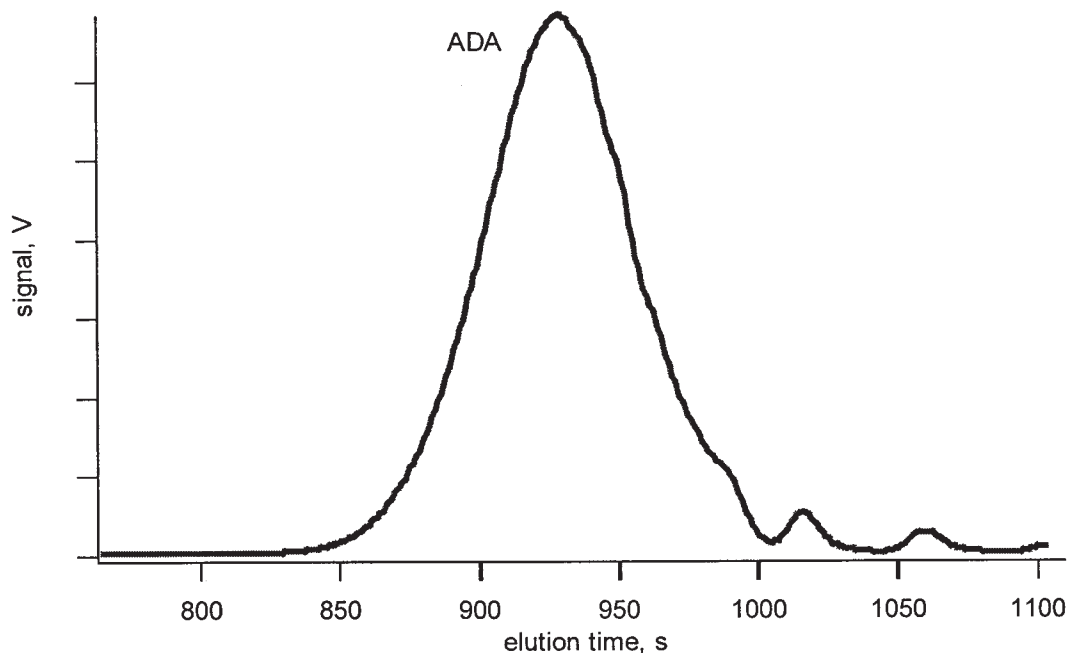


Figure 1 GPC traces of UAO[d].

tion of each fraction will require a deconvolution of overlapping individual bands.) M_w obtained in this work differs from the real values. (GPC was calibrated by polystyrene standards.³ M_w measured by our technique is higher than the actual M_w up till $\sim 60\%$.³ For

example, for P, we got a reading $M_w = 5500$, where as a manufacturer reports $M_w = 4006$ g/mol (based on OH# = 28.0).

Table I presents measured properties of liquid and cured UAOs.

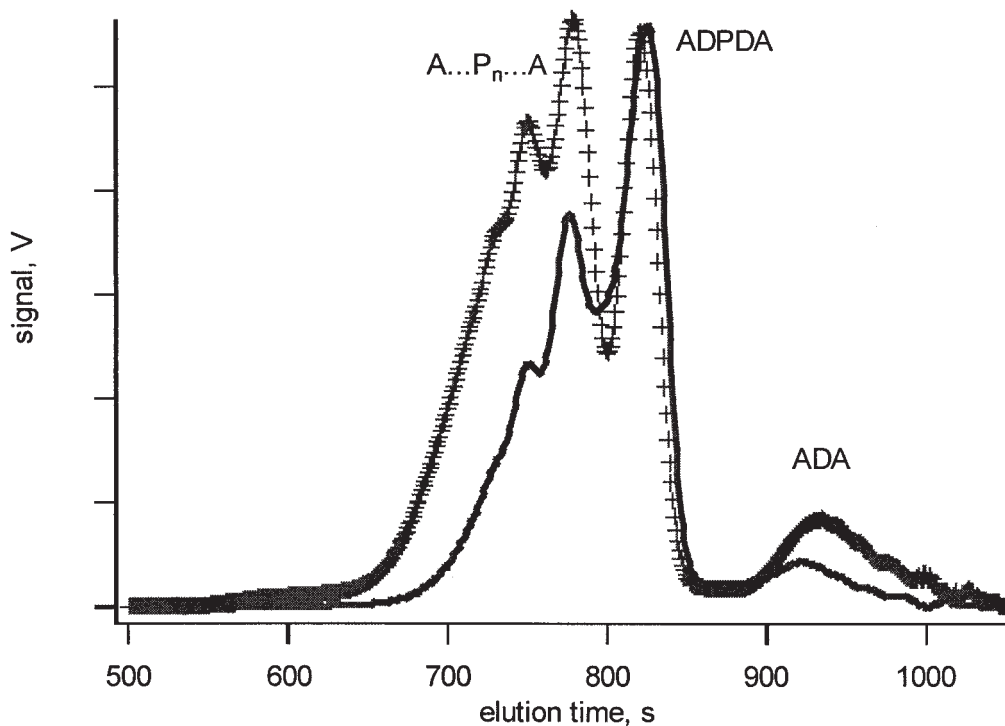


Figure 2 GPC traces of UAO[2a] (solid line) and of UAO[2b] (line with markers).

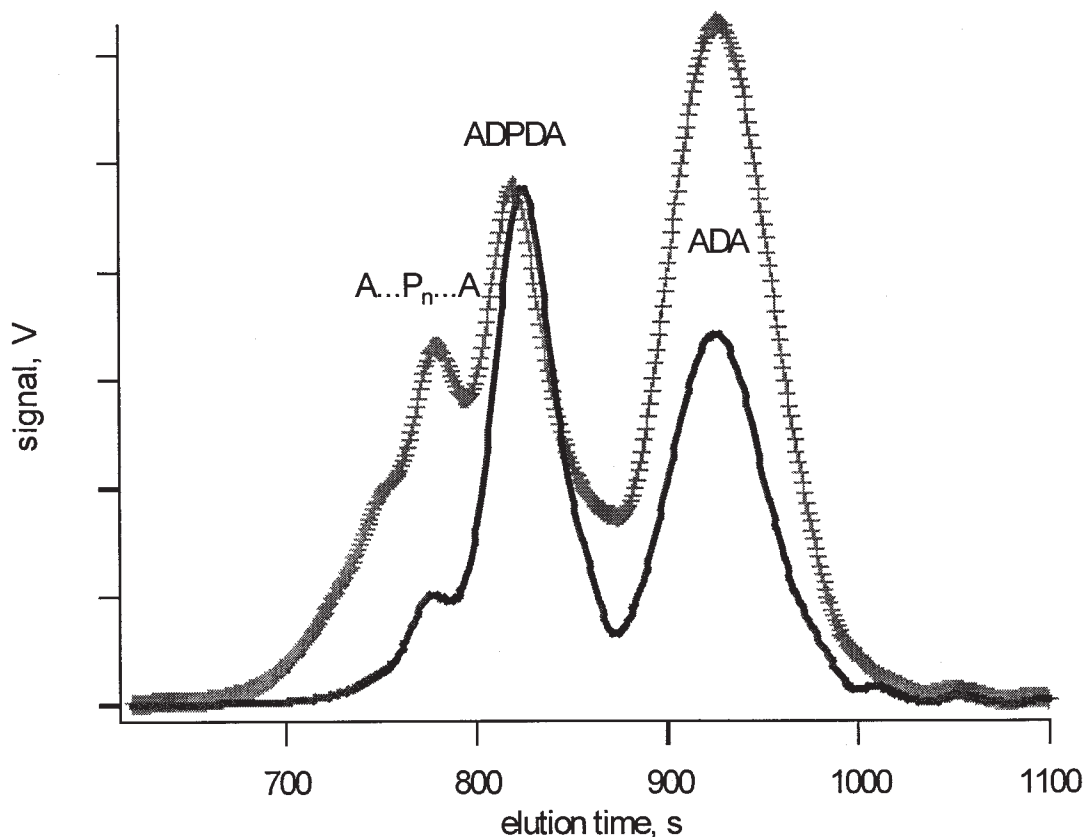


Figure 3 GPC traces of UAO[6] (solid line) and of UAO (line with markers).

DISCUSSION

GPC of UAO[d] consists of one peak with a maximum at 925 s (Fig. 1). Minor peaks, which appear on Figure 1, are probably due to impurities.

GPC trace of UAO[2a] (Fig. 2) demonstrates the presence of ADA at 925 s in a low level, cf. Table I. A peak at 780 s is ascribed to ADPDA. The next peak next at shorter time (750 s) left and a vague shoulder (~ 730 s) are ascribed to $A \dots P_n \dots A$. In other words, $A \dots P_n \dots A$ includes a compound with two P in its

structure $A \dots P_2 \dots A$ (at 750 s) and a shoulder, cf. Figure 2. The shoulder can be safely ascribed to a molecule with three Ps. It is quite possible that there are other chain-extended products in a lower concentration with four or more Ps. These products do not manifest themselves on a GPC trace.

It is assumed in the literature that ADPDA is the main, or even the only product of UAOs syntheses, cf. refs 1,2. Data of Table I demonstrates that it is not necessarily the fact, and reactions (1) and (2) are the

TABLE I
Measured Properties of Liquid and Cured UAOs^a

Oligomer	Equivalents P : D : A ^b	η, cP^c	ADPD A (%)	$A \dots P_n \dots A$ (%)	ADA (%)	M_w (g/mol)	MWD	Elongation at break (%) ^d	Tensile strength at break (MPa) ^d	Tensile modulus (MPa) ^d	T_g (°C)
UAO[2a]	1 : 2 : 1	22,500	50	40	10	11,800	2.2	83	1.3	3.2	-55
UAO[2b]	1 : 2 : 1	39,000	24	68	8	31,000	1.1	97	1.3	2.2	-57
UAO[6]	1 : 6 : 5	11,250	46	7	47	5400	2.4	71	2.6	3.9	-56
UAO	1 : 6 : 5	17,750	28	21	51	6700	3.3	108	4.5	3.8	-56
UAO[d]	0 : 1 : 1	4250	0	0	100	1500	1.3	79	10.5	12.3	20

^a - Determination errors of: values M_w , MWD, and η is $\approx 10\%$; values of elongation to break and moduli is $\approx 15\%$; and of T_g is $\pm 1^\circ\text{C}$.

^b - Cf. this section in the text for details.

^c - At 25°C.

^d - At ambient temperature.

simplification of the total process.³ A usual for the coating industry oligomer with $D : P = 2 : 1$, UAO[2a], has only 50% ADPDA, and $A \dots P_n \dots A$ is in a comparable level of 40%. UAO[2b] with the same $D : P = 2 : 1$ has $A \dots P_n \dots A$ as the main component (68%), and ADPDA accounts only for 24%.

There is a straightforward way to decrease a contribution of $A \dots P_n \dots A$ relative to ADPDA. An increase of $[D]/[P]$ ratio in reaction 1 leads to an increase of relative concentration of DPD and consequently to a decrease of relative concentration of $A \dots P_n \dots A$. Figure 3 presents GPC of UAO[6]. An increase of a ratio of equivalents of D to P from 2 in UAO[2a] to 6 in UAO[6] leads to a decrease of a ratio $[A \dots P_n \dots A]/[ADPDA]$ from 0.8 to 0.15 (Table I). A large excess of D vs. P is used in UAO[6]. That excess of D is consumed in a reaction with A leading to a high level of ADA in UAO[6] of 47% (Fig. 1, Table I). A high enough ratio $D : P$ will lead to UAO consisting of ADA and ADPDA without chain-extended products. Peebles calculated M_n , the concentration of ADA, and some other parameters of UAOs. Unfortunately, that approach based on formal kinetics is applicable only to diluted solutions, and it cannot be applied to the formation of neat oligomers.⁶

Another method of a reduction of $[A \dots P_n \dots A]$ is a reverse addition, i.e., an addition of A to D first. This method was studied in the work of Swiderski and Khudyakov.³

All UAOs containing P consist of three components ADPDA, $A \dots P_n \dots A$, and ADA. Table I presents approximate contributions of these components into the synthesized UAOs, cf. the Experimental Section. Partial properties can be ascribed to each component, and the observed properties can be satisfactorily considered as a weighted sum of these three components (Table I).

η of UAO is essentially, but not exclusively in general, determined by their M_w , cf. Table I. UAO[d] with the lowest M_w has the lowest η . UAO[2b], which has the lowest contribution of UAO[d], has the highest η . η of UAO is approximately a weighted average of η 's of UAO[2a] and UAO[d]. Therefore, an addition of D to P is recommended to get high M_w and high η oligomers. On the contrary, and addition of P to D and the highest possible $D : P$ are recommended for getting low M_w and low η oligomer.

Couples UAO[2a] and UAO[2b], UAO[b] and UAO[6] were prepared out of the same reagents taken in the same amounts, cf. Table I. At the same time, GPC traces of UAOs of each pair are quite different, cf. Figures 2 and 3 and Table I. That observation is instructive, and it helps in preparation of UAO with desired properties by selecting a mode of addition.

Tensile properties of the studied UAOs do not differ drastically (Table I). UAO[d] has the highest T_g , the highest tensile strength, and the highest modulus

among five studied UAOs. Such properties are expected for oligomer with the lowest M_w . UAO[b], which has the largest contribution of UAO[d] (51%), has the second highest strength and modulus. (Moduli of UAO[b] and UAO[6] are equal within experimental error of their determination, cf. Table I). UAO[2b] with the highest contribution of $A \dots P_n \dots A$ has the lowest tensile modulus (Table I).

T_g 's of four oligomers practically coincide with each other (Table I). Such low T_g 's are characteristic for elastomers. Figure 4 presents a temperature dependence of shear storage modulus G' . It follows from the Figure 4, that these cured materials have a very distinct rubbery plateau. Probably, T_g of a soft segment P essentially determines T_g .

Cyclic polyurethanes are expected byproducts in UAO formed by a reaction D with P.³ However, we did not get experimental evidence of formation of nonacrylated polyurethane.

Many cured UAOs meet user expectation providing coatings with required properties: tough or soft and elastic, abrasion resistant, with good adhesion to a substrate, impact resistance, etc. Evidently, such UAOs have a good balance ADPDA, $A \dots P_n \dots A$, and ADA, which lead to desired properties of cured coatings. $A \dots P_n \dots A$ imparts softness to a coating and/or lead to a higher elongation-to-break. ADA imparts hardness. (As a reminder, we discuss in this article simple UAOs made out of three ingredients, and P and D are difunctional.)

Mode of addition of three reagents (A, D, and P) taken in the same amounts essentially affects composition of a formed UAO, its M_w , η and properties of the cured films. It was demonstrated in this work that addition of D and A in two portions or in a total amount of each at once leads to oligomers with essentially different properties, cf. UAO[6] and UAO[b] (Table I, Fig. 3).

Thus, a purposeful manipulation with ways of addition of the same three compounds allows affecting properties of the formed UAO. Adjusting of D to P ratio is another way of changing M_w and optimization other properties of UAO.

Additional experiments with a number of common P's, D's, and a common capping agent 2-hydroxyethyl acrylate at high $[D]/[P]$ ratio resulted in a brittle coating due to the presence of ADA in a high concentration. ADA with 2-hydroxyethyl acrylate is a solid compound at room temperature. It is necessary to use oligomeric A like Tone M100 or other to get elastomers.

CONCLUSIONS

The studied UAOs were products of a reaction between three selected reagents D, P, and A. A mode of addition of these reagents leads to different relative

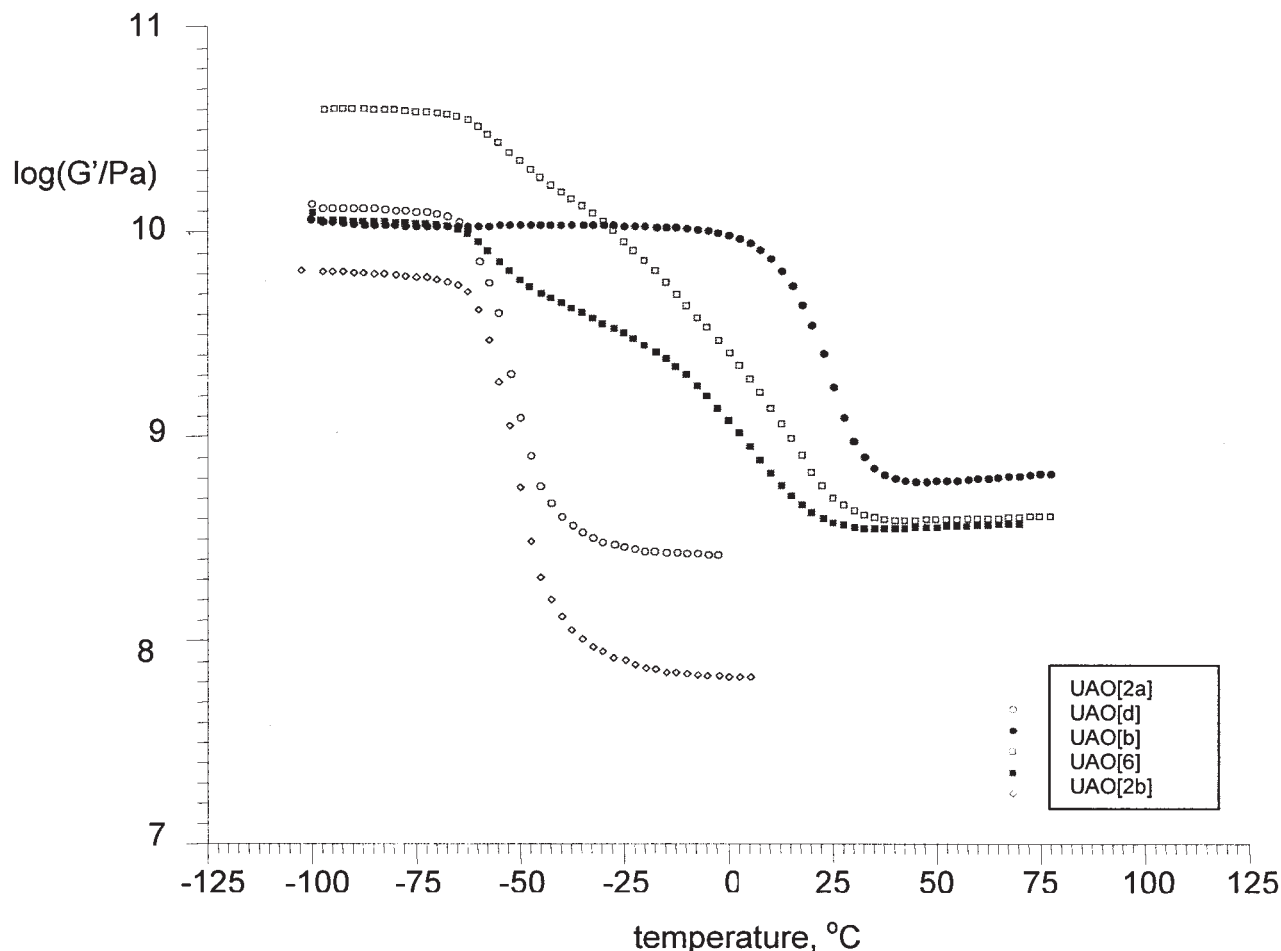


Figure 4 Dependence of G' vs. temperature.

contribution of three main products ADA, ADPDA, and a chain-extended product $A \dots P_n \dots A$, where $n \geq 2$. ADA was prepared as an individual compound, and its properties were studied. Properties of these three products make approximately additive contributions into observed properties of liquid and cured UAOs. ADA has the lowest η , whereas $A \dots P_n \dots A$ has the highest. A purposeful synthesis of UAO with one or another contribution of ADA and $A \dots P_n \dots A$ allows getting the required M_w and η . It was found that η is proportional to M_w of UAO, which is a nontrivial observation for oligomers with hydrogen bonds. All oligomers have an evident rubbery plateau on a temperature dependence of G' .

We stress that ADPDA is not the only product of UAO formed by any type of addition as described earlier and in the work done previously.³ Moreover, it is not necessarily the main product. Low M_w compounds ADA and high M_w compounds $A \dots P_n \dots A$ are inevitably formed in all UAOs. A relative contribution of $A \dots P_n \dots A$ decreases with an increase of

$[D]/[P]$ ratio; ADA has the highest tensile modulus, and an UAO with the largest contribution of $A \dots P_n \dots A$ has the lowest tensile modulus. Examples of these of work demonstrate how to prepare UAO with expected properties.

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