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# APPLIED CHEMISTRY

# Synthesis and Properties of Urethane Acrylate Oligomers: Direct versus Reverse Addition

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Common urethane acrylate oligomers can be synthesized by one of two modes of addition. A polyol can be terminated on each end with diisocyanate and then capped with a hydroxy functional acrylate, *direct addition*, or a diisocyanate can first be reacted with a hydroxy functional acrylate, and that product can be used to terminate a polyol, *reverse addition*. This paper demonstrates how the mode of addition of the same reagents essentially changes the viscosity and molecular weight of the synthesized urethane acrylate oligomer.

## Introduction

Urethane acrylate (UA) coatings represent one of the most widely used types of radiation-curable coatings. Two methods of synthesizing UAs are known; the methods are often referred to as *direct addition* and *reverse addition* in this paper.

The direct addition technique comes from more traditional urethane chemistry: the diisocyanate (D) is first reacted with a polyol (P, commonly difunctional) often at an equivalent ratio of two isocyanate groups to one hydroxyl group, forming a urethane prepolymer; the resulting material is blocked with a hydroxy functional acrylate (A).[1] The idealized direct addition reaction with a difunctional polyol is

$$2D + 1P \rightarrow DPD; \quad DPD + 2A \rightarrow ADPDA \quad (1)$$

The reverse addition technique takes a different approach. In this approach, the diisocyanate (D) is first reacted with a hydroxy functional acrylate (A) in a manner forming the maximum amount of a desired product that has one acrylate group and one isocyanate group. This material is reacted with the proper amount of polyol (P) to consume the remaining isocyanate groups. The idealized reverse addition reaction with a difunctional polyol is

$$2A + 2D \rightarrow 2AD; \quad 2AD + 1P \rightarrow ADPDA \quad (2)$$

Evidently, both reactions as they are presented above, lead to the same product. This product should have the lowest viscosity, which is important for UA coatings. Thus, it is desirable to have the highest possible yield of ADPDA in reactions such as eqs 1 and 2. ADPDA, formed as the only product, should have the same molecular weight distribution (MWD) as a starting polyol P.

The statement "for symmetrical diisocyanates, the order of addition is unimportant"[2] seems to be logical at first glance. However, this paper examines the differences in the real products formed with participation of both symmetrical and nonsymmetrical diisocyanate (D). We ran three pairs of chemically identical UAs, with each pair based on a different diisocyanate; the only difference between the members of each pair was the method by which they were prepared: one by direct addition and the other by reverse addition.

## Experimental Section

**Reagents.** The P used was difunctional poly(propylene glycol) with a reported $M_w$ = 1000 g/mol (PolyG 20-112 from Arch with hydroxyl number 112); A was 2-hydroxyethyl acrylate from San Esters. P probably has a small fraction of monofunctional polyol, but $M_w$ (or an equivalent weight of 500 g/mol or a hydroxyl number) determines the amount of reactive OH groups. We used three D's: tolylene 2,4-diisocyanate (TDI from Bayer; TDI is a known mixture of two isomers); isophorone diisocyanate (IPDI from Rhodia), and 4,4′-methylenebis-(cyclohexyl isocyanate) ($H_{12}$MDI or Desmodur W from Bayer). We used a catalyst of urethane synthesis[3] dibutyltin dilaurate (Fascat 4202 from Atofina) at a level of 500 ppm based on the polyol.

We used also monofunctional isocyanate 2-isocyanoethyl methacrylate, abbreviated herein as DMA from Aldrich. 4-Methoxyphenol (from Eastman) was used as an inhibitor of spontaneous polymerization at a 500 ppm level based on the mass of a final acrylate-containing product. All compounds were used as received.

**Devices.** Properties of the products were analyzed with gel permeation chromatography (GPC), which gave us number-average and weight-average molecular weights ($M_n$ and $M_w$); MWD = $M_w/M_n$. The GPC device consisted of a Waters column heater and degasser, a Perkin-Elmer 200 series pump and RI detector, a Rheodyne 7125 injector, and two consecutive Polymer Laboratories PLgel Mixed D columns packed with polystyrene/divinylbenzene. GPC was calibrated with polystyrene standards, and only relative values $M_w$ ($M_n$)

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**Table 1. Properties of UAs Based on TDI**

|  | $\eta$, cP at 50 °C | $M_w$, g/mol | MWD |
|---|---|---|---|
| direct addition | 12750 | 3740 | 1.72 |
| reverse addition | 8700 | 2920 | 1.63 |

**Table 2. Properties of UAs Based on IPDI**

|  | $\eta$, cP at 50 °C | $M_w$, g/mol | MWD |
|---|---|---|---|
| direct addition | 8100 | 3590 | 1.59 |
| reverse addition | 4850 | 2910 | 1.58 |

**Table 3. Properties of UAs Based on $H_{12}MDI$**

|  | $\eta$, cP at 50 °C | $M_w$, g/mol | MWD |
|---|---|---|---|
| direct addition | 23 750 | 5990 | 2.61 |
| reverse addition | 14 125 | 4500 | 2.08 |

of the studied oligomers have meaning. Values $M_w$ ($M_n$) obtained in this work may differ from the real values up until ca. 60%. The carrier solvent was tetrahydrofuran, and the column temperature was set to 40 °C. This device was attached to a computer running PENelson Turbochrom software via a PENelson series 900 interface. The total elution time of GPC was 22 min; the low molecular mass compound ADA (cf. below) was included in a calculation of the reported $M_w$. Infrared (IR) spectra were reviewed, paying particular attention to the peak at 2230 cm$^{-1}$ (NCO) and watching for the completeness of the reaction via extinction of isocyanate and the overlays of each pair. The IR spectrometer was a BioRad Fourier transform infrared model FTS 155 with a ZnSe HATR accessory from Pike Technologies. This device was directly connected to a computer with BioRad WinIR software. The viscosity ($\eta$) was measured with a Brookfield RVT with a small adapter (spindle SC4-15 and cup 7R) connected to a Neslab circulating water bath at 50 or 25 °C.

## Results

We have prepared six similar batches with the same P and three different D (cf. the Experimental Section) by direct and reverse additions. All six materials were run in two stages according to eqs 1 and 2 with subsequent reactions with the straightforward stoichiometric molar ratio of 1:2:2 = P:D:A (cf. eqs 1 and 2). A synthesis of each of the six batches was repeated two or three times using the same raw materials in order to verify reproducibility of the data.

All six syntheses were performed in a very similar way. The reactions were run at 60 °C, and the reactants were added in a manner to keep the reaction temperature under 65 °C. The first stage of the reaction took place over a period of 2 h and the second, final, stage over a period of 8 h. All syntheses started with D, the catalyst, and the inhibitor in the pot, and the remaining ingredients were added.

It was informative to endcap P not with a diisocyanate capable of chain extending and cross-linking (cf. below) but with a monoisocyanate (DMA). A reaction with DMA can result in only one product, DMA−P−DMA. We ran the reaction under similar conditions to all other syntheses with a proper ratio of ingredients (2:1). It was instructive to check whether MWD and $\eta$ change upon such an extension of P. Two syntheses of DMA−P−DMA out of the same raw materials were performed.

Tables 1−4 present the properties of UA oligomers obtained in this work.

The determination error of values in Tables 1−4 is ca. 10%. A comparison of the viscosities and $M_w$'s of all
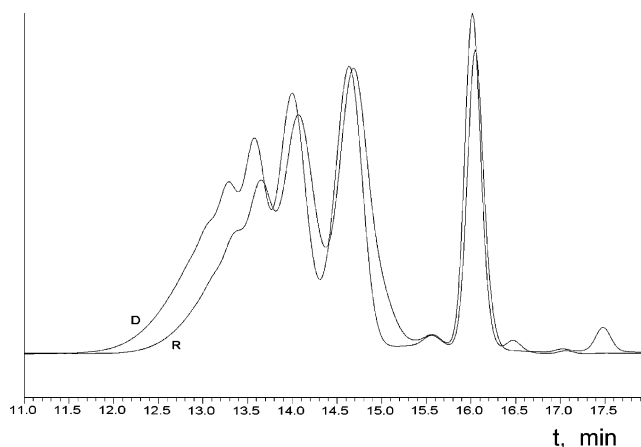


**Figure 1.** GPC traces of products obtained in direct (**D**) and reverse (**R**) additions. D was $H_{12}MDI$.
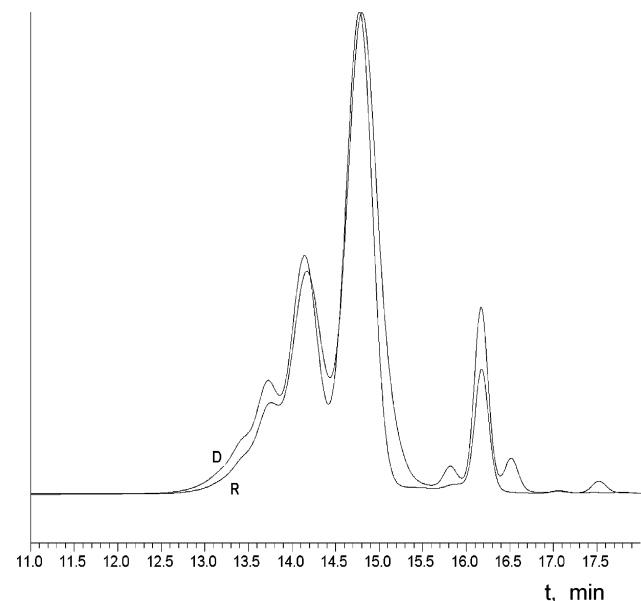


**Figure 2.** GPC traces of products obtained in direct (**D**) and reverse (**R**) additions. D was IPDI.

**Table 4. Properties of Polyol and Urethane Methacrylate Based on DMA**

|  | $\eta$, cP at 25 °C | $M_w$, g/mol | MWD |
|---|---|---|---|
| P | 125 | 1550 | 1.05 |
| DMA−P−DMA | 1125 | 1750 | 1.06 |

batches (Tables 1−3) made by direct and reverse additions out of the same raw materials (cf. Results section) demonstrated that $\eta$ ($M_w$) of the oligomer prepared by reverse addition is lower by 30−40% (20−30%) than $\eta$ ($M_w$) of the oligomer prepared by direct addition out of the same chemicals.

The IR spectra were examined for each pair of experiments. Direct and reverse addition techniques produced overlay IR spectra for each pair. All syntheses performed in this were complete by IR (less than 0.2% residual NCO).

The tables do not give enough information from the GPC to see all changes in molecular formation; an examination of chromatogram overlays is desirable. Figures 1−3 present overlays of the GPC traces obtained from the oligomers made with the three D used. The curves were normalized to the concentration of the product of most interest, ADPDA. In Figures 1−3, **D** stands for the direct addition and **R** for the reverse
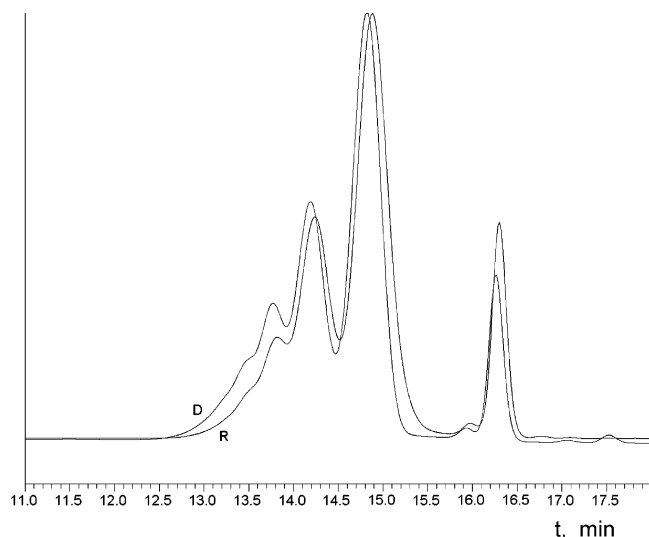
**Figure 3.** GPC traces of products obtained in direct (**D**) and reverse (**R**) additions. D was TDI.

addition. A compound with the largest retention time was identified in independent experiments as low-$M_w$ ADA (Figures 1−3).

## Discussion

Experimental data in Table 4 confirm the expected. MWD of a polyol does not change within an error of its determination by endcapping P with monofunctional species. $M_w$ of a bigger oligomer, DMA−P−DMA, is evidently higher than $M_w$ of P, by ca. 10% according to our measurements (Table 4). We used GPC calibrated with polystyrene (cf. the Experimental Section). A correct difference in $M_w$ of P (1000 g/mol according to a supplier) and DMA−P−DMA (1312 g/mol) is ca. 30%. Interestingly, $\eta$ of DMA−P−DMA with its hydrogen bonds between urethane links is almost 10 times higher than $\eta$ of P (two batches were prepared; cf. the Results section).

Apparently, not only $M_w$ and MWD but also the number and type of hydrogen bonds between urethane oligomers essentially affect $\eta$.

A situation with D + P + A is much more complicated. It follows from the data of Tables 1−3 that $\eta$'s of the reverse addition products are markedly less than $\eta$'s of their direct addition counterparts. Lower $\eta$ is expected from products with lower $M_w$ and lower MDW (Tables 1−3), with all other conditions being equal (especially the number and type of hydrogen bonds).[4] Analysis of the data of Tables 1−3 leads us to the conclusion that reactions (1) and (2) result in different products and/or in different relative concentrations of products.

We have presented reactions (1) and (2) above as idealized or simplified reactions, which lead to one the final product. It is evident that reaction 2D + 1P does not result in only one intermediate product DPD (reaction 1) but results in more complex intermediates such as DPDPD, etc. A simple consideration of the stoichiometry and of the material balance allows us to make some solid conclusions. First, we remind the reader that all isocyanate groups are consumed in direct and reverse syntheses, as it was proven by IR (cf. the Results section). Second, we will assume, for brevity, that stoichiometric coefficients in eqs 1 and 2 are the number of moles of charged reagents. A formation of intermediates DPD, DPDPD, and similar more complex products

in the direct addition still results in the formation of 2 equiv of isocyanate as in the idealized reaction (1). All isocyanate groups are consumed in the reaction with A, and one gets in the direct addition ADPDA, ADPDPDA, and similar more complex products. The GPC trace (Figure 1a) demonstrates several peaks and a shoulder, which evidently indicate the formation of several products of different $M_w$.

It is possible to form complex intermediate linear structures (e.g., DPDP, DPDPDP, DPDPDPDP, etc., cf. above), which are formed as a part of the prepolymer in the direct synthesis. These structures, having a hydroxyl functionality at one end and an isocyanate functionality at the other, have the ability to react with themselves, forming polyurethane oligomers.

We will denote polyurethane oligomers as [DP], and their formation should take place. It is known that a reaction of 1D + 1P leads to the formation of polyurethane.[5] Despite the expected formation of [DP], residual isocyanate groups will be still endcapped by A.

Now let us consider a real reverse synthesis (eq 2a,b). The first stage of the reaction results in two products:

$$2A + 2D \rightarrow (2 - 2x)AD + xADA + xD \qquad (2a)$$

where $x < 1$. A subsequent reaction of the products of reaction (2a) with P leads to

$$(2 - 2x)AD + xADA + xD + 1P \rightarrow products \qquad (2b)$$

The products evidently include ADA as well as [DP], ADPDA, and more complex structures with no loose unreacted NCO or OH. However, contrary to direct addition (2D + P), in the reverse addition we have a situation of [D] < [P] (or $x < 1.0$). The latter inequality results in a lower probability to have extension by D and to form ADPDPDA and similar more complex structures. In fact, data of Figures 1−3 (trace **R** vs the corresponding trace **D**) support these observations: one can notice a lower relative contribution of high-$M_w$ compounds. That is the most probable reason for the lower $\eta$ in the case of the reverse addition.

The following fact ensues simply from the stoichiometry of the **R** and **D** processes: a higher concentration ADA in the R process is accompanied by a lower concentration of high-$M_w$ products with two and more P, or a lower concentration ADA in the **D** process is accompanied by a higher concentration of high-$M_w$ products with two and more P.

Peebles[6] calculated $M_n$, the concentration of ADA, and some other parameters of polyurethanes formed by the addition of polyol and a chain extender to diisocyanate. Unfortunately, that approach based on formal chemical kinetics is applicable only to diluted solutions, and it cannot be applied to the formation of solventless oligomers.[1]

It was demonstrated above (Table 4) that endcapping of P with a monofunctional terminal group does not change MWD because of the evident inability of DMA to promote chain growth. In the case of ADPDA or ADPDPDA and similar more complex compounds, one should expect that their retention time and a peak shape do not depend on the method of their preparation. In reality, that is not true (cf. traces **R** and **D** of each of Figures 1−3). Let us consider ADPDA as the simplest compound. In a direct synthesis, ADPDA is formed (along with other products) in the reaction of P + D with a subsequent reaction with A. ADPDA in the reverse

synthesis is formed in the reaction of P + DA. MWD of ADPDA formed in the direct and reverse syntheses can be somewhat different because of the different reactivities of D and DA toward alcohols P and toward different individual P molecules of different $M_w$. That is why one observes the same shape and the same retention time for ADA but slightly different shapes and maxima for peaks, which should be ascribed to ADPDA (cf. traces **R** and **D** on each of Figures 1−3).

Now, peaks containing two, three, and more P's (Figures 1−3) are most probably of somewhat different structure because of the reason described above and because of different contributions of [DP] with two and more P's.

A comparison of GPC traces **D** and **R** in Figures 1−3 allows one to conclude that the relative concentrations of moieties with several P's are lower in the products of *reverse addition* compared to the products of *direct addition*. This fact evidently explains the lower $\eta$ of the reverse addition products (Tables 1−3). Thus, contrary to the suggestion of ref 2, even for symmetrical D like H$_{12}$MDI, a sequence of additions is important, and direct and reverse additions lead to different relative concentrations of products.

Data of Tables 1−3 demonstrate that measured properties of UA oligomers prepared with the same P depend on D. The effect of D on the structure and properties of UA oligomers was studied in detail in ref 7.

## Conclusion

The results of the present work demonstrate an essential difference in viscosities and molecular weights of UA oligomers prepared from the same reagents by a different mode of addition. The UAs made by *reverse addition* have lower $\eta$'s and $M_w$'s than their *direct addition* counterparts. This held true for all three isocyanates used, independent of any differential reactivity. Care and thought should be set forth before choosing a procedure when synthesizing UAs. The expected product ADPDA can be maximized by a diligent process development.

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