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Synthesis and Characterization of Model Urethane Compounds[†]

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ABSTRACT: Model urethanes with a narrow distribution are useful in the investigation of structure–property relationships in polyurethanes. Normal random copolymerization leads to statistically distributed segment sizes. A new method has been developed to synthesize model urethanes based on 4,4′-methylenebis[phenyl isocyanate] (MDI) and 1,4-butanediol (BDO). First, one of the hydroxyl groups in BDO is protected by trityl chloride and then the other is chloroformated. After reaction with 4,4′-diaminomethylenebis[benzene] (MDA) and product separation, an asymmetrical intermediate, $HO(CH_2)_4OC(=O)NHC_6H_4CH_2C_6H_4NH_2$ (BM′NH$_2$), is isolated. BMB $[(HO(CH_2)_4OC(=O)NHC_6H_4)_2CH_2]$, formed by reaction of MDI with singly protected BDO and followed by deprotection, can be chloroformated and coupled with BMNH$_2$, making B(MB)$_3$. The same sequence of reactions using the B(MB)$_n$ as starting materials can be used to synthesize B(MB)$_{n+2}$. Increasing insolubility of the reactants B(MB)$_{n+2}$ in THF for $n > 3$ probably necessitates the use of a more powerful solvent such as dimethyl sulfoxide. GPC, elemental analysis, and infrared spectroscopy all indicate that pure monodisperse compounds B(MB)$_n$, where n = 1, 2, and 3, can be readily produced in multigram quantities suitable for coupling into multiblocks with polyether soft segments. Melting points of the oligomers precipitated from solution increased from 130 to 237 °C as n increased from 1 to 5. However, thermal treatment of the precipitated samples produced several other polymorphs with different melting temperatures.

I. Introduction

The multiblock polyurethanes generally consist of a "hard" segment capable of forming a strong hydrogen-bonded network with a high T_g that alternates with polyether or polyester "soft" segments of much lower T_g. The development of high mechanical strength in a material with a continuous rubber phase requires that the hydrogen-bonded segments, whether crystalline or not, phase separate from the soft phase in a finely dispersed fashion obtaining a high density of physical cross-links.[1–6] When reaction injection molded (RIM) urethanes are polymerized at low catalyst concentrations, hard segments are thought to phase separate before they can react with polyether and reinforce the material.

Several types of inhomogeneously distributed morphology and/or hard-segment crystal structures are readily revealed (in RIM urethane parts) by the presence of multiple DSC endotherms[4] whose relative magnitude depends on processing conditions. Similarly, X-ray crystallography of urethanes with an amorphous polyether soft segment reveals the presence of a disordered phase and several more ordered phases which are obviously associated with the spherulitic structures.[7] In the RIM of 4,4′-methylenebis[phenyl isocyanate] (MDI) chain extended with 1,4-butanediol (BDO) and multiblocked with poly(ether glycol),[8] the spherulitic phase can be minimized by using sufficiently high reaction temperature or catalyst level to rapidly produce high molecular weight and viscosities. Consequently, upon rapid cooling, each molecule is incorporated with minimal intermolecular diffusion into many small dispersed crystalline structures. However, given enough time at sufficiently high temperature below the maximum melting temperature (~240 °C), this structure can reorganize to yield spherulites.

The chemical microstructure is also important. Even though gel permeation chromatography (GPC) reveals that the overall molecular length increases with reaction temperature, the hard-segment length distribution in the multiblock probably also changes.[8] The latter factor would obviously have an influence on the phase separation process and, unluckily, is impossible to determine by GPC. The ideal solution, selective chemical cleavage of the polyether segment, and subsequent isolation of the hard segment blocks, is a formidable challenge.

Clearly, model urethanes, for example, hard blocks with a known length and triblocks and multiblocks with monodisperse hard segments and soft segments can be very valuable in (1) defining the phase diagram of different chain microstructures at various stages of RIM processing, and thus, the influence of morphology on reaction kinetics and (2) providing model morphologies from which especially definitive structure–property correlations could be made. The attempts to prepare such model materials for properties studies are few because of the careful and laborious procedures that are required, often rivaling poly(amino acid) synthesis.

Harrell[9] made materials of monodisperse hard-segment length which were based on piperazine and butanediol hard segments coupled with poly(tetramethylene ether) soft segments and observed significant increases in modulus, tensile strength, and elongation over materials of wider hard-segment length distribution. However, there was no hydrogen bonding possible between the molecules. Wilkes[10] used the reaction of MDI with excess BDO followed by fractionation to prepare the first two hard blocks with known length; however, no physical properties were measured. Camberlin et al.[11] obtained monodisperse hard block from preparative GPC but the quantity of product (~10 mg) was sufficient only for DSC measurements. Additionally, the products were capped by alkyl end groups, preventing further reaction to obtain model urethane block copolymers.

In this paper we will describe the synthesis of urethane hard segments which are made from commercial urethane intermediates, namely 1,4-butanediol (BDO, GAF, 99% pure) and 4,4′-methylenebis[phenyl isocyanate] (MDI, Rubicon Chemicals, 99% pure). The procedure is designed to make multigram quantities of hard segments with reactive ends capable of reacting with polyethers to produce block copolymers.

II. Synthesis

The model compounds we desire to make are listed below: B(MB)$_n$, where n = 1, 2, 3, or 5; B, $HO(CH_2)_4O$ at the end of the compound, $O(CH_2)_4O$ otherwise; M, $O{=}CNHC_6H_4CH_2C_6H_4NH{-}C{=}O$; M′, $O{=}CNHC_6H_4CH_2C_6H_4$.

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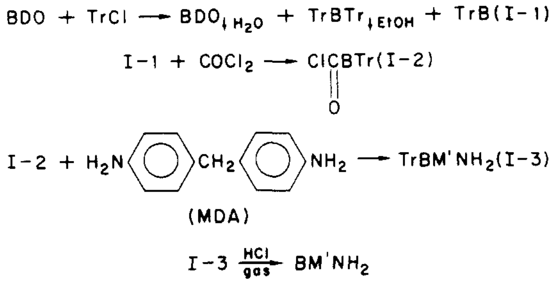
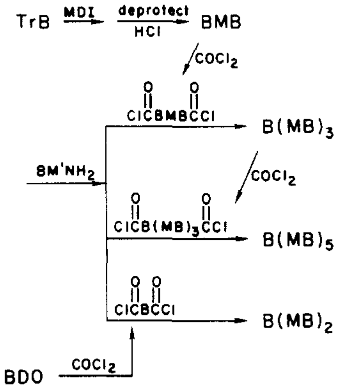
Scheme I
Synthesis of BM'NH$_2$ Intermediate



Scheme II
Synthesis of Hard Segments



The difficulty in making narrow hard blocks is that normal random reaction of MDI with BDO produces a broad distribution of lengths which have similar solubilities or cocrystallize, especially at higher molecular length. As in the stepwise synthesis of proteins, we utilized the method of protecting active groups by selecting an appropriate masking reagent to build up desired chain length and deprotecting the product. This process was immensely facilitated through isolation of an asymmetric intermediate 4-(1-hydroxybutyl)-4'-aminodiphenylmethane (BM'NH$_2$). The hydroxyl end of BM'NH$_2$ remains as the end group of the hard segments which can be later chloroformated and reacted with amino-terminated soft segment. The amino group of BM'NH$_2$ can be used to lengthen hard segments with chloroformated dialcohol ends.

The other intermediate required is a monoprotected BDO. Because of BDO's difunctionality, a diprotected product will also be produced. This byproduct can be separated from the desired monoprotected intermediate by using the greater solubility of the latter in ethanol. Triphenylmethyl chloride (TrCl) is chosen as a protecting agent[12] because (1) TrCl reacts with hydroxyl-containing compounds rapidly and quantitatively, (2) the byproducts can be separated easily, and (3) the trityl-ether bond is sensitive to weakly acid conditions which do not affect the urethane bond and hence allow quantitative recovery of the protected hydroxyl group.

In general, the important aspects of the synthesis strategy are that all separations are done on low molecular weight intermediates which can be then coupled and/or deprotected to well-defined products by quantitative reactions involving no further solvent-nonsolvent separations.

A. Synthesis Route for BM'NH$_2$. This low molecular weight compound can be obtained in pure form with high yield by recrystallization (Scheme I).

I-1. A solution of 44 g (0.16 mol) of triphenylmethyl chloride (TrCl) (99%+, Aldrich) and 176 mL of pyridine was added dropwise into a solution of 58 g of BDO (0.65 mol) and 135 mL of pyridine at 80–90 °C and reacted for 4 h at that temperature. The pyridine was evaporated and 150 mL of ethyl alcohol added to precipitate the diprotected byproduct (TrBTr) while excess BDO was removed by adding water. Crude I-1 was extracted by ethyl ether and recrystallized in ethyl alcohol and water (3/2 v/v), mp 69–71 °C. The yield of monoprotected product was 65%, the remaining being diprotected and unprotected product. Anal. Calcd: C, 83.13; H, 7.23; O, 9.29. Found: C, 82.96; H, 7.26; O, 9.63.

I-2. A solution of 10 g of the monoprotected alcohol (I-1) (0.03 mol) in 30 mL of ether and 4.04 g of triethylamine (0.04 mol) was added dropwise into 8.9 g of liquid phosgene (0.09 mol) at -5 °C over 1 h. A white solid (Et_3N–HCl) was filtered out and washed with ether. The remaining phosgene solution and ether extract were combined and then evaporated to yield 11 g (98% yield) of the monochloroformated product (I-2).

I-3. Dry tetrahydrofuran (THF) (10 mL) and 1.5 g of 4,4'-diaminomethylenebis[benzene] (MDA) (Aldrich 98%, acidified with HCl–MeOH, cleaned with activated charcoal, reprecipitated with base and recrystallized) were placed in a three-neck flask. A solution of 10 mL of THF and 3.1 g of I-2 and a solution of 10 mL of water and 0.83 g of sodium carbonate were then added dropwise into the flask simultaneously at a temperature below 20 °C under continuous stirring, allowed to react for 30 min, and finally separated into water and organic phases. The latter was washed with water three times, the organic solvent evaporated, and the product dried to 4 g solid I-3 (90% yield). A total 4 g of the monoprotected key intermediate I-3 was dissolved in 20 mL of methylene dichloride and dry HCl gas was bubbled through the solution for 30 min until a yellow solid compound (BM'NH$_3^+$Cl$^-$) separated and could be collected by filtration. In order to purify the product, 20 mL of water was added to dissolve the hydrochloride salt, thus facilitating separation of insoluble materials. The aqueous solution was neutralized by ammonium hydroxide to precipitate the amine which was subsequently dried and washed with benzene, filtered, and dried once more. To complete purification crude BM'NH$_2$ was dissolved in 10 mL of ethyl acetate and gaseous HCl added to precipitate the hydrochloride salt which was then dissolved in 20 mL of water to facilitate filtering of insoluble materials. When the clear water solution was neutralized with 0.5 M sodium hydroxide and allowed to stand for 0.5 h, a white solid appeared and was filtered and washed with water to obtain a pH 6–7. The above procedure was repeated once more to complete purification. After drying under vacuum at 50 °C, 0.5 g of BM-NH$_2$ (25% yield) mp 94–95 °C was obtained. Anal. Calcd: C, 68.79; H, 7.01; N, 8.92; O, 15.28. Found: C, 68.87; H, 7.14; N, 9.90; O, 15.14.

B. Synthesis Route for B(MB)$_n$ (Scheme II). BMB. A total of 3.3 g of the monoprotected BDO (I-1, 0.01 mol), 1 g of MDI (0.004 mol), and 40 mL of dry THF were mixed at 60 °C for 6 h. After evaporation of all the THF with subsequent addition of 30 mL of methylene dichloride, dry HCl gas was bubbled through the solution for 30 min at 25 °C. The solid residue was collected and washed with ether. This crude BMB was recrystallized twice from methanol and water to make 1 g of product (58% yield), the rest being lost in recrystallization.

B(MB)$_2$. Chloroformated BDO was prepared by reacting BDO with liquid phosgene in a mole ratio of 1:4 in THF at 3 °C for 30 min and further at 10–25 °C for 2 h. A solution of 0.32 g of sodium carbonate in 10 mL of water and a solution of 0.65 g of chloroformated BDO in 10 mL of dry THF were added dropwise simultaneously into a solution of 0.2 g of BM'NH$_2$ in 10 mL of THF at 15 °C over 1 h with stirring. After separation of the water phase, the organic phase was washed with water and the crude product precipitated by evaporation of the organic phase. The solid was washed with methanol–1,4-dioxane and dried under vacuum at 80 °C; 0.2 g of B(MB)$_2$ was collected. The additional 0.05 g expected was probably lost in handling.

B(MB)$_3$. Phosgenation of BMB was carried out in the same way as the BDO chloroformation. A solution of 50 mL of THF and 0.88 g of chloroformated BMB and a solution of 50 mL of water and 0.34 g of sodium carbonate were added dropwise simultaneously into a solution of 50 mL of THF and 1 g of BM'NH$_2$ below 10 °C. After reaction for 2.5 h, 100 mL of water was added to precipitate the product which was washed with 1,4-dioxane and methanol and dried. A total of 1 g of B(MB)$_3$ was collected (60% yield).

B(MB)$_5$. A total of 500 mg of B(MB)$_3$ was dissolved in 100 mL of THF and then added dropwise over a 0.5-h period into liquid phosgene stirred while held at -5 to 0 °C. The mixture was then stirred for 2 h at 10 °C. When the suspension finally cleared, the remaining phosgene and THF were driven off and 500 mg of product was collected.

Table I
Elemental Analysis of Synthesized Oligomers

	% C	% H	% N	% O
BMB				
exptl	64.35	6.89	6.53	22.10
calcd	64.17	7.02	6.50	23.30
$B(MB)_2$				
exptl	65.22	6.67	7.48	20.44
calcd	65.44	6.54	7.27	20.76
$B(MB)_3$				
exptl	65.73	6.33	7.57	20.32
calcd	65.95	6.31	7.47	20.18
$B(MB)_5$				
exptl	66.16	6.25	7.78	19.68
calcd	66.37	6.15	7.82	19.66

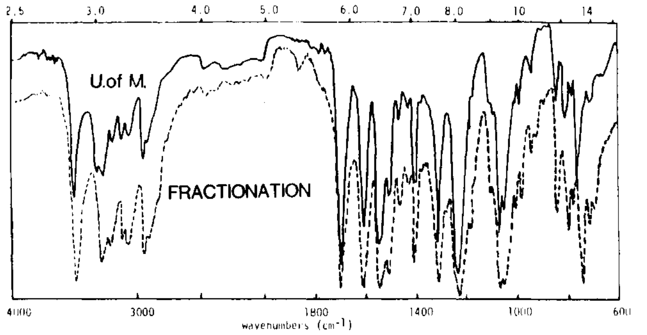


Figure 1. Infrared spectra of sequentially synthesized BMB (—) and BMB prepared by fractionation (- - -)[10] (KBr pellet).

A solution of 500 mg of chloroformated $B(MB)_3$ in 20 mL of THF and a solution of 100 mg of sodium carbonate in 10 mL of water were added simultaneously dropwise into a solution of 250 mg of $BM'NH_2$ in 10 mL of THF below 20 °C and reacted for 2 h. After reaction, 200 mL of water was poured into the mixture to precipitate the crude $B(MB)_5$ which was washed with water and methanol and dried to yield 500 mg of $B(MB)_5$ (70%).

III. Results and Discussion

The elemental analysis of all the hard-segment oligomers synthesized agrees well with the predicted compositions (Table I). The infrared spectrum of the BMB produced by sequential synthesis is nearly identical with the BMB produced by solvent–nonsolvent fractionation (Figure 1). A complicating factor, however, is the polymorphism of BMB which could affect the solid-state infrared spectrum significantly because of different hydrogen-bonded networks in each crystal structure.[13] Identical IR spectra could be obtained only from BMB crystals precipitated from solution under identical conditions. For example, the spectra in Figure 1 are seen only when BMB is rapidly precipitated from a basic solution.

The GPC of the oligomers was obtained on a Waters 150-C operating with four 60-s silanized glass bead columns in sequence at 85 °C in dimethylformamide (DMF) solvent. The column resolution under these conditions is superior for low molecular weight species permitting, for example, separation of dibromo and unbrominated *N*-methylcarbazole.[14]

The GPC traces appearing for $B(MB)_n$ ($n = 1$, 2, and 3) are clearly monodisperse (Figure 2). Unfortunately $B(MB)_5$ contains 20% of $B(MB)_4$, most probably originating from an incomplete reaction of $B(MB)_3$ and phosgene in the THF solution. A plot of the log of the molecular weight vs. retention volume is quite linear for these oligomers (Figure 3). The suspected $B(MB)_4$ also falls on this line, lending further credence to its assignment. Incomplete chloroformation of $B(MB)_3$ is also a possibility considering the decreased solubility of this material. In order to alleviate this problem we are presently studying better solvents for the hard-segment oligomers of higher molecular weight, e.g., dimethyl sulfoxide, a solvent also unreactive to $COCl_2$.

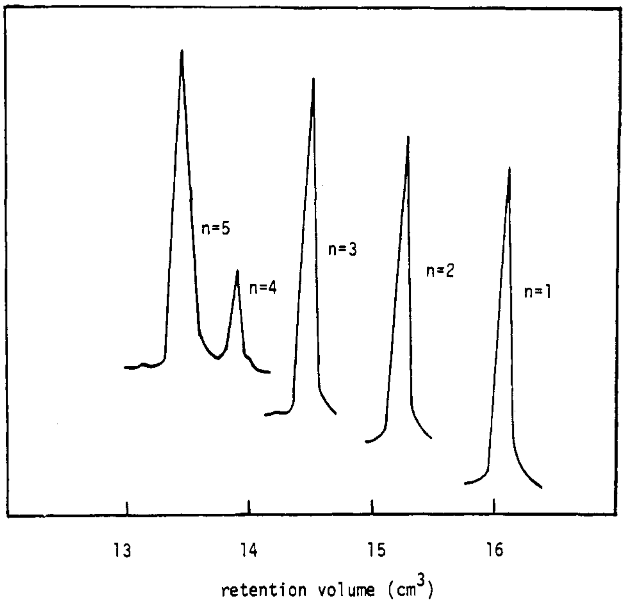


Figure 2. GPC results of model hard segments $B(MB)_n$.

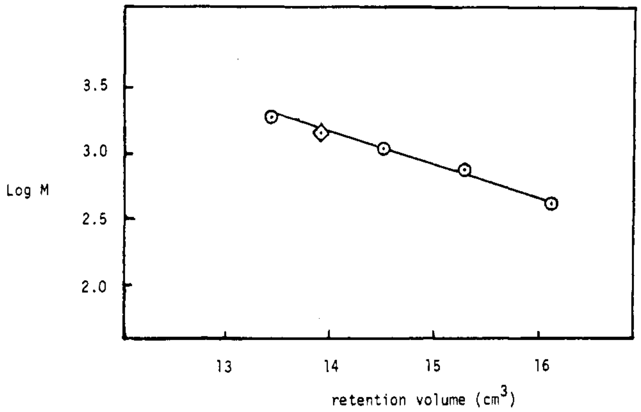


Figure 3. Relationship of molecular weight to retention volume, 85 °C, DMF, four silanized glass bead columns.

One would expect that the melting point T_m of the oligomers would increase with increasing molecular weight as a consequence of increased crystal thickness. The only complication would be the onset of chain folding which would of course limit the crystal thickness. Preliminary electron diffraction data from some of our collaborators[15] in fact verify that the chains are extended at least up to $n = 3$.

In order to test the expected melting point trend, 5 mg of the oligomer was placed in a hermetically sealed aluminum pan, whereupon the relative heat capacity vs. temperature was obtained in a Mettler TA3000 DSC at a scan rate of 10 °C/min.

The thermal behavior of the as precipitated material was quite complicated, although the melting point did increase with increasing chain length as expected (Figure 4); $B(MB)_3$ provided the most straightforward thermogram in that only one sharp endotherm was observed at 213 °C. A small exotherm that appeared in the scan of $B(MB)_2$ at 159 °C was indicative of some amorphous component in the as precipitated material. The melting endotherm for $B(MB)_2$ at 183 °C was broader than either the BMB transition at 118 °C or the $B(MB)_3$ transition at 213 °C. Electron diffraction evidence for two $B(MB)_2$ crystal structures of virtually the same melting point has recently

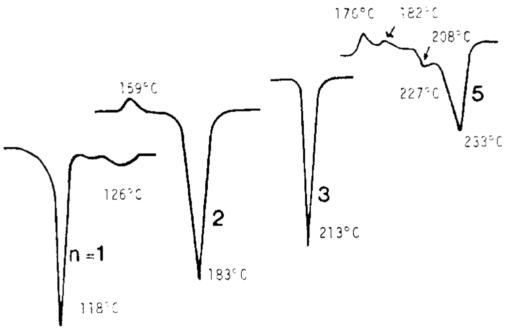


Figure 4. DSC of as-precipitated hard-segment oligomers showing multiple endotherms and crystallization exotherms.

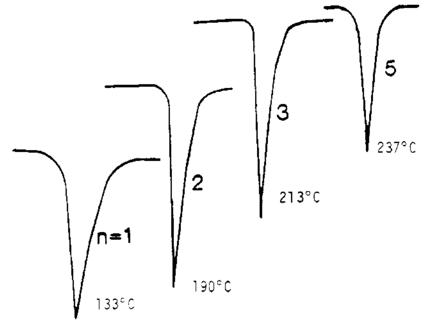


Figure 5. DSC of annealed oligomers showing melting point increase and only single endotherms.

been obtained,[15] a result certainly in line with the breadth of the 183 °C peak.

B(MB)$_5$ is only partially crystalline as precipitated and consequently shows two crystallization exotherms at 176 and 182 °C. The first endotherm at 208 °C is followed by a broad melting at 233 °C which actually consists of two components, a principal component melting at 233 °C and a minor component at 227 °C. Conceivably the lower melting peak could originate from a mixed crystal of B(MB)$_4$ and B(MB)$_5$. This melting point might be significantly suppressed relative to higher melting B(MB)$_4$ and B(MB)$_5$ crystals due to incorporation of chain-end defects. The relationship of the exotherms to the endotherms is being investigated.

We attempted to simplify and improve the crystalline order of the oligomers by annealing B(MB)$_n$ (n = 1, 2, 3, and 5) at 125 °C/30 min, 180 °C/30 min, 170 °C/2 h,[15] and 214 °C/30 min, respectively (Figure 5). B(MB)$_3$ was completely unaffected by annealing below its T_m, the endotherm width and position remaining the same. Little change in the peak position for B(MB)$_2$ was seen but the endotherm sharpened considerably, suggesting the elimination of the crystal polymorph or the development of more monodisperse crystal sizes. The melting point and endotherm breadth of BMB increased significantly upon thermal treatment as the 118 °C crystal form transformed into another polymorph at 133 °C whose presence was foreshadowed by the appearance of a small endotherm at 126 °C in the as precipitated material. The large changes that are seen in wide-angle X-ray d spacings after annealing under the same conditions[15] using the same -100% purity BMB and the dependence of the IR spectra upon precipitation conditions support polymorphism in BMB. Annealing B(MB)$_5$ completely removed the low-temperature endotherm, leaving only the higher temperature 237 °C melting peak. Cocrystallization of B(MB)$_4$ and B(MB)$_5$ is certainly one explanation for the appearance of only one transition after annealing. However, chemical reactions such as transurethanization are also possible above 180 °C.[11]

Table II
Thermal Transition Data on Oligomers

n^a	MW	T_m, °C	H, J/g
1	430	118	73
		126	
1′		133	147
2	770	183	102
2′		190	132
3	1110	213	142
5	1790	208	55
		227	
		233	
5′		237	88

^{a} n, as precipitated; n', annealed.

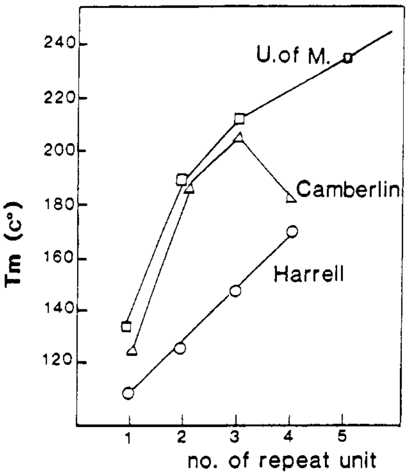


Figure 6. Comparison of the melting points of hard-segment oligomers synthesized by different routes. In general the melting point increases with the number of repeat units.

The heats of fusion for the annealed and unannealed oligomers are shown in Table II. The most obvious fact is the significantly smaller heat of fusion for the B(MB)$_5$. Incorporation of chain-end defects in a crystal containing a multimodal distribution could certainly explain these results, as could a lower degree of crystallinity. The absence of X-ray data on B(MB)$_5$ precludes us from preferring either mechanism at the present time.

The heat of fusion for BMB also increases substantially from 73 to 147 J/g upon annealing. This large increase must be a consequence of the formation of a much more ordered crystal, melting at 133 °C. The heat of fusion differences between the lower melting and higher melting crystals could originate from a lower degree of crystallinity in the as precipitated BMB which showed a heat capacity change typical of a T_g at 85 °C, actually rather close to the 110 °C T_g of the high molecular weight amorphous polymer.[8] This suggests that the breakup of disordered intermolecular hydrogen bonds and not chain ends contributes most to the heat capacity change at T_g.[16]

Our well-annealed oligomers have a heat of fusion more than 50 J/g larger than those obtained by Camberlin et al.[11] for an equivalent length. For example, their R(MB)$_2$MR, R = OC_2H_5, OC_8H_{17}, which would be similar to our B(MB)$_3$ has a heat of fusion equal to 94 and 98 J/g vs. our 132 J/g. Conceivably all of their samples were of the more poorly packed crystal structure that we observed in some of our as precipitated samples.

The melting point of the oligomer of chain length n = 5 already approaches the melting point of the polydisperse, high molecular weight (MB)$_n$ copolymer, 248 °C[8] in Figure 6. This result is not in agreement with the work of Camberlin et al.,[11] who find that the melting point of R(MB)$_3$MR is less than R(MB)$_2$MR (Figure 6). However, this discrepancy might be explained by the differences in end groups. In our case hydrogen bonding with OH end groups might contribute to the heat of fusion. The melting points of our $B(MB)_n$ (n = 2, and 3) are in excellent agreement with the same oligomers recently synthesized by Eisenbach and Gunter.[17]

One should be cautious in using DSC T_m's to compare model compound purity, however. Recently, we have found that $B(MB)_3$ can exhibit three crystalline polymorphs melting between 185 and 240 °C.[18] The additional polymorphs are produced by annealing above the transurethanization temperature (~180 °C) where GPC shows significant molecular weight broadening.

Longer oligomers, such as $B(MB)_7$, are of interest in determining when chain folding, if any, will occur in MDI–BDO based poly(ether urethanes). The competition between this crystallization mechanism and fringed micelle crystallization will clearly affect the overall morphology of the solid.

Our synthesis scheme also includes within it the option of adding hard segments, one at a time, to a chloroformated polyether polyol to form a triblock by the reactions

Step 1

$$ClC(=O)-(OCH(CH_3)CH_2)_x-C(=O)Cl + BM'NH_2 \rightarrow$$

Step 2

$$BM(OCH(CH_3)CH_2)_xMB \xrightarrow{COCl_2} ClC(=O)BM(OCH(CH_3)CH_2)_xMBC(=O)Cl$$

repeat 1 and 2 to build a triblock

Triblocks so formed may then be reacted with MDI to form multiblocks with monodisperse hard and soft blocks ideal for morphological and mechanical properties investigations. So far we have synthesized $BM(OCH(CH_3)CH_2)_xMB$ and $BMBM(OCH(CH_3)CH_2)_xMBMB$ but have been unable to make a monodisperse $(BM)_3(OCH(CH_3)CH_2)_x$ triblock. Again, just as in the production of pure hard segment blocks, we suspect that we will be able to solve this problem by attempting the reactions in a better solvent.

Another variation on this scheme which allows us to be sure of the hard segment length in a multiblock is to chloroformate a hard block of known length and react it with amine-terminated polyethers which have recently become available for RIM polymerizations.

IV. Conclusions

We have developed a synthetic scheme to produce gram quantities of model urethane oligomers of the form $B(MB)_n$. High-resolution GPC has verified that the oligomers are monodisperse for n = 1, 2, and 3. As expected, with increasing oligomer length, the melting point increases and approaches the melting point observed for high molecular weight hard segment. Well-annealed samples with n = 1, 2, and 3 all have similar heats of fusion per gram, suggesting a similar crystalline hydrogen-bonded structure. The low solubility of $B(MB)_3$ and $B(MB)_4$ in $COCl_2$–THF precludes the synthesis of monodisperse $B(MB)_5$ or higher oligomers. Increasing the reactant solubility, for example, by use of $COCl_2$–$(CH_3)_2SO$, is expected to solve this problem and work is presently in progress using this solvent.

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Registry No. MDA, 101-77-9; BDO (chloroformated), 2157-16-6; BDO·MDI (3:2 adduct), 79802-39-4; BDO·MDI (4:3 adduct), 93061-42-8; BDO·MDI (4:3 adduct) bis(chloroformate), 93061-43-9; BDO·MDI (6:5 adduct), 93061-44-0; 4-(triphenylmethoxy)-1-butanol, 38257-94-2; 4-(triphenylmethoxy)butyl chloroformate, 90331-89-8; 4-hydroxybutyl [4-(4-aminobenzyl)phenyl]carbamate, 93061-45-1; bis(4-hydroxybutyl) (methylenedi-*p*-phenylene)dicarbamate bis(chloroformate), 93061-46-2.

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