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POLYURETHANES FROM 4,4'-DIPHENYLMETHANE DIISOCYANATE AND POLY(OXYETHYLENE) GLYCOLS. I. PREPARATION AND GENERAL PROPERTIES

Argyris S. Vatalis[a]; Aristides H. Kehayoglou[b]

[a] Physics and Material Technology laboratory, T.E.I. of Kozani, Kozani, Greece [b] Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

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POLYURETHANES FROM 4,4'-DIPHENYLMETHANE DIISOCYANATE AND POLY(OXYETHYLENE) GLYCOLS. I. PREPARATION AND GENERAL PROPERTIES

Argyris S. Vatalis[†] and Aristides H. Kehayoglou*

Laboratory of Organic Chemical Technology, Department of Chemistry,
Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

ABSTRACT

Linear polyurethanes (PU) from 4,4'-diphenylmethane diisocyanate and an equimolar quantity of poly(oxyethylene) glycol (PEG) of various molecular weight (106, 200, 400, 1000, 2000, and 4000) were obtained by polymerization using 4-methylpentanone-2 as solvent at 115°C. Alternative reaction conditions and melt polymerization were also applied. Samples were characterized by elemental analysis, solubility, I.R. spectroscopy, DSC (T_m, T_g), [n] and $\bar{M}_n$ (osmotic). The results are correlated with the molecular weight of PEG and discussed.

Key Words: Linear polyurethanes of poly(oxyethylene) glycols and diphenyl-methane diisocyanate; Degree of polymerization.

INTRODUCTION

Several studies [1-10] have been published in recent years on the investigation of the morphology and properties of polyurethanes, which are dependent on the hard to soft segments ratio of the polymeric chain.

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*Corresponding author.

[†]Present address: Physics and Material Technology Laboratory, T.E.I. of Kozani, 50100 Kozani, Greece.

The possibility of long soft blocks, like poly(oxyethylene) chains, which can undergo crystallization can lead to modification of the properties of the materials and influence the aging of the system. In polyurethane elastomers, it is difficult to identify and study the effects of various factors on the generation of crystalline phases within the soft block. Nevertheless, the use of linear polyurethanes of high crystallinity of the soft block should be accessible models for study.

Furthermore, in this work, a series of new linear polyurethanes are prepared from 4,4'-diphenylmethane diisocyanate (MDI) and an equimolar quantity of crystalline poly(oxyethylene) glycols (PEGs) of various molecular weight ($\overline{MW}$:000, 2000, and 4000), of liquid poly(oxyethylene) glycols ($\overline{MW}$: 200 and 400) and di(oxyethylene)glycol ($\overline{MW}$: 106.12). The properties dependence of the PUs on the length of the soft segments are studied.

The results of the preparation of these polyurethanes, by identical and alternative reaction conditions, and their characterization data (solubility, elemental analysis, I.R. spectrum, T_m, T_g, $[n]$, $\overline{M}_n$, $\overline{DP}_n$, %) are presented and discussed.

EXPERIMENTAL

Materials

4,4'-Diphenylmethane diisocyanate (MDI), practical grade (Bayer, m.p. 38°C) and poly(oxyethylene) glycols (PEG) of average molecular weight ($\overline{M}_n$) 200 ± 10, 400 ± 20, 1000 ± 50 (Sigma) and 2000 ± 200, 4000 ± 400 (Aldrich) and di(oxyethylene) glycol (Merck) (PEG 106) were used, after drying at vacuum (2mm Hg, 70°C, 12 hours) or by addition of active (400°C, 3 hours) molecular sieves 3A (Merck). Solvents 4-methylpentanone-2 (MP) (Riedel-de Haen, b.p. 115°C) and dioxane (Merck, b.p. 101°C) were used after distillation in the presence of potassium hydroxide and then addition of molecular sieves.

Polymerization

Polymerizations were conducted under the same concentration of reactants (approx. 90 g/100 ml of MP) and identical reaction conditions (115°C, 2 hours) in a three-necked round-bottom flask equipped with stirrer, dropping-funnel and condenser with tube with phosphorous pentoxide for protection from moisture. The vessel was heated in a silicone oil bath and all reactants and reaction vessel were dried intensively before use.

A typical polymerization procedure was as follows: The half quantity of MP and the required amount of MDI were placed in the flask. To this rapidly stirred suspension, the required amount of PEG dissolved in the remaining quantity of solvent was added gradually. The reaction was heated at 115°C for 2 hours. After the oil bath was removed and the reaction mixture cooled (50-60°C), about 10 ml of methanol was added to convert the end-isosyanate groups into urethane groups, under stirring for half an hour. The remaining methanol and solvent were removed

in a vacuum evaporator and the product was dried in a vacuum oven at 60°C. The reaction product with PEG106, PEG200, and PEG400, assigned respectively as polyurethane PU106, PU200, and PU400 was entirely washed with methanol under stirring to remove non-polyurethane contaminants. After filtration, the extracted product was dried in vacuum as done previously, and used for characterization, while the filtrate was evaporated, dried, and the percentage extracted matter was determined.

In addition, some polymerizations were also conducted under alternative reaction conditions (time, solvent, etc).

Characterization

Solubilities of samples (approx. 0.1 g) in various solvents (5 ml) were assessed visually at ambient temperature or at an elevated temperature.

Thin layer chromatography tests were carried out on silica gel aluminum plates (Riedel-de Haen) using an eluting solution of chloroform: methanol: water (3:25:12 v/v) for 3 hours. Drops of 0.5–1% w/v solutions of PUs and corresponding PEGs in tetrahydrofuran were applied alongside. An orange color was developed by spraying a modified Dragendorff solution [11, 12], which was prepared by mixing 5 ml of each solution; (a) and (b) with 20 ml of acetic acid and 70 ml water. Solution (a): 0.8 g of bismuth subnitrate, 10 ml of acetic acid and 40 ml water; (b): 40% (w/v) aqueous solution of potassium iodide.

Polyurethanes compositions were determined by elemental analysis performed on samples dried over P_2O_5 in vacuum using a Perkin-Elmer model N240 analyzer.

I.R. absorption spectra were recorded over the range 4000-650 cm^{-1} using a Perkin-Elmer 281B instrument. Data were taken using films (PU200) or compressed melt between NaCl plates (PU106, PU400, PU1000, and PU2000) or using KBr pellets containing 0.3% sample by weight (PU106, PU2000, and PU4000).

Melting points were determined by the use of: (a) a Kofler-Reichert hot-stage polarizing microscope, taking the disappearance of birefringence as the highest temperature of melting; (b) a Shimadzu DSC-50Q differential scanning calorimeter calibrated with indium. Recordings were run at heating and cooling rates of 10°C min^{-1} on samples of *ca* 10 mg. The maximum peaks of endotherms or minimum of exotherms were taken as the melting or crystallization temperatures, respectively and the average temperatures of three samples of each polymer were reported.

Glass transition temperatures were determined by the use of the above differential scanning calorimeter.

Intrinsic viscosities were obtained for solutions of the polymers in freshly distilled dioxane (PU200, 400, 1000, 2000, 4000) or dimethylformamide (PU106) at 25°C with Ubbelohde viscometers.

Number average molecular weights ($\bar{M}_n$) were determined with a membrane osmometer (Knauer) using regenerated cellulose membrane (Sartorius) and

tetrahydrofurane (THF) for PU200, 400, 1000, 2000, and 4000, and dimethylformamide (DMF) for PU106 as solvents.

RESULTS AND DISCUSSION

The physical state of prepared polyurethanes were as following: PU106 was a white powder, PU200 a relatively hard solid, PU400 a soft and sticky material, PU1000 a very soft material, while PU2000 and PU4000 were brittle solids.

Solubility tests in a series of solvents with increasing solubility parameters [δ: 7.4-23.4 (cal/cm^3)$^{1/2}$], as ether, 4-methylpentanone-2 (MP), tetrahydrofurane (THF), chloroform, acetone, p-dioxane, dimethylformamide (DMF), ethanol, methanol and water showed: PU106 to be soluble only in DMF; PU200, and PU400 soluble also in THF and dioxane; moreover, PU1000 soluble in chloroform, acetone, ethanol, and hot methanol, while in cold and hot water gave a turbid mixture; on the contrary PU2000 and PU4000 were also soluble in hot MP, cold methanol and water, like their corresponding monomers PEG2000 and PEG4000. The differences in solubility are attributed to the decreasing content of aromatic MDI urethane segments and hydrogen-bondings, with a consequent increase of the content of the hydrophilic oxyethylene segments from PU106 to PU4000.

Purification of the products PU106, PU200, and PU400 to remove non-polyurethane contaminants, was carried out by treatment with methanol, whereas a similar purification for PU1000, PU2000 and PU4000 was not possible as no relevant selective solvent could be found and their yield was considered 100%.

The polymerization yields for PU106, PU200 and PU400, after extraction with methanol, were high (99.7%, 98.8, and 89.2, respectively), since the corresponding methanol dry extract was found to be 0.3, 1.2, and 10.8%, increasing in amount with increasing the molecular weight of PEG.

Thin layer chromatography under the applied conditions showed the absence of unreacted PEG, for the extracted with methanol PU106, PU200 and PU400. However, the crude (not extracted) PU1000, PU2000 and PU4000 showed the presence of a low amount of lower molecular weight derivatives up to the trace area of the corresponding PEG.

The determined R_f for the samples of PEG200 – PEG2000 (0.78, 0.66, 0.56, and 0.25, respectively) showed a good linear relationship vs. their mean molecular weight, while that for PEG4000 (R_f: 0.11) showed a positive deviation.

The results of the elemental analyses of prepared polyurethanes (PU106–PU4000) were in good agreement with those expected for their chemical composition (I):

$$H-[(OCH_2CH_2)_m-O-\underset{O}{\overset{O}{C}}-NH-\bigcirc-CH_2-\bigcirc-NH\underset{O}{\overset{}{C}}]_n-OCH_3$$

(I)
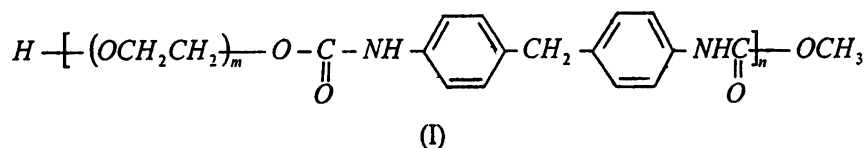
where m=($\overline{MW}_{PEG}$ – 18)/44.05 (*oxyethylene unit*).

I.R. spectra of all prepared samples were characteristic of polyurethane structure [1730–1725 cm^{-1} ν (C=O) free, 1700-1710 cm^{-1} ν (C=O) bonded, 1533–1528 cm^{-1} (amide III, ν(C– N) + δ(N – H)) and 1235–1232 cm^{-1} ν(C-O) [13] and that of ether bonding of PEGs (1115–1100 cm^{-1}) and phenyl rings of MDI (1600–1590 cm^{-1} and 1417-1410 cm^{-1})]. The absorption intensity of the bonded urethane imide groups (3330–3310 cm^{-1} ν (N – H), ignoring a relevant contribution of a negligible amount of hydroxyl-end groups (bonded~3200 cm^{-1}) of PU macromolecules, appeared decreasing with increasing the molecular weight of the PEG used, while that of free imide groups (3500–3490 cm^{-1}) was increasing, respectively. Determination of the ratio of absorption intensity [14] for the bonded (D_b) and free (D_f) imide groups showed imide groups to be highly bonded (~94%) in PU106 and PU200 (D_b/D_f: 16.4 and 16.2, respectively), mostly bonded (62 –54%) in PU400–PU2000 and less bonded (~43%) in PU4000 (D_b/D_f: 0.74).

The melting points (T_m) determined by two methods are in good agreement and given in Table 1.

The DSC-endotherms of polyurethanes showed a main fairly sharp melting and remelting peak except that of PU1000 of the first-run which showed one more low peak, like a sample of the PEG1000 used. Such multiple endotherms may be due to the existence of two different crystalline modifications [15] or in this case to two crystal distributions different in size and/or perfection in the initial sample. The DSC- thermograms also showed that all the polymer melts were thermally stable up to 300°C under the scanning conditions.

PU106 showed the highest melting point and T_g(DSC) and a very small remelting endotherm curve revealing a relatively lower crystallization rate than that of PU1000 to PU4000. Unlike them, PU200 and PU400 were amorphous based on their DSC thermograms. The melting points of PU1000 through PU4000

Table 1. Characterization Data of Prepared Polyurethanes

| Polyurethane | Kofler m.p. | DSC | | | | | | | |
		T_m[a] (°C)	T_c[b] (°C)	$T_{m'}$[c] (°C)	T_g (°C)	[η] (dl g^{-1})	$\overline{M_n}$	$\overline{DP_n}$	p
PU106	179–182	181.4	—[d]	175.3	94	0.35	20400	57	0.982
PU200	—[e]	—[e]	—[e]	—[e]	40	0.26	18900	42	0.976
PU400	—[e]	—[e]	—[e]	—[e]	−11	0.17	13500	21	0.952
PU1000	28–40	31.3	2.4	25.9	−47	0.16	10300	9	0.889
PU2000	49–51	51	25	47.1	−82	0.16	14400	6	0.833
PU4000	56–59	57.6	34.5	55.6	−89	0.15	13500	3	0.667

[a]Melting temperature of the initial sample (maximum peak of first-run)
[b]Crystallization temperature
[c]Remelting temperature
[d]No crystallization curve was scanned
[e]Amorphous

showed an increase with increasing the molecular weight of the PEG used and these points were slightly lower than those of the respective PEGs. These m.p. depressions must be due to the sparse presence of the urethane linkages in these PUs.

On the contrary, the glass transition temperature values (DSC) of PU106 to PU2000 were found to decrease with an increasing the chain length of the PEG used and slightly afterwards to PU4000. This, is attributed to the increase of the chain flexibility in the amorphous fraction of polyurethanes with the increase of the length of the soft segments (PEGs).

Intrinsic viscosity [*n*] values (Table 1) were also found decreasing significantly with increasing the chain length of PEG for PU106, PU200, and PU400 and insignificantly afterwards for PU1000 to PU4000. In this comparison, the [*n*] value of PU106 determined in DMF was assumed to be practically similar as if in dioxane (insoluble), since the approximate PU200 showed the same [*n*] value in dioxane or DMF.

PU200 samples prepared by extending the polymerization time from 2 to 5 hrs or recovering the PU product by an alternative process, precipitating it in water, showed the same [*n*] and molecular weight ($\bar{M}_n$) values respectively (Table 1). However, PU200 prepared by a reduced reactants concentration (45% instead of 90% w/v) showed a lower [*n*] value (0.20 in comparison to 0.26 dL/g - Table 1), attributed to the dilution of the reactive end–groups.

For PU2000, extending the polymerization time (2 to 5 hours), resulted in an increase of [*n*] value from 0.16 to 0.20 dL/g. Hence, a lower reaction rate of PEG2000 than that of PEG200 was seen, probably due to the higher molecular weight of the glycol, yielding lower concentration of reactive end–groups.

PU2000 prepared using as polymerization solvent dioxane resulted in almost identical [*n*] and $\bar{M}_n$ values with that using as solvent methylpentanone (Table 1).

The number average molecular weights ($\bar{M}_n$) of the prepared PUs (Table 1), determined osmometrically, were used to calculate their degree of polymerization ($\overline{DP}_n$) (represented by the symbol *n* in the formula I), by the equation:

$$(\overline{DP}_n) = (\bar{M}_n - 31.03)/(\bar{M}_{PEG} + 250.25)$$

where 31.03 and 250.25 are the molecular weights of methanol and MDI, respectively.

$\overline{DP}_n$ values for PUs (in integers in Table 1) vs. their PEG molecular weights showed a regular relationship curve, as about [*n*] values, with an initial deep fall from that of PU106 up to PU1000 and following then a linear slight reduction up to that of PU4000. The very low $\overline{DP}_n$ values of PU1000, PU2000, and PU4000 (9, 6, and 3, respectively) suggests they are best characterized as oligomers (or actually as "polymeric oligomers" because of their polyoxyethylene segments) or as prepolymers. In addition, the indications of the TLC tests, it is concluded that a part of derivatives initially formed from two or somewhat more molecules of the reactants (MDI and PEG) could not react further to afford more polyurethane mol-

ecules, contributed to low mean DP_n values. This reduced reactivity of high molecular weight PEGs to afford high PUs under various conditions, is attributed to the decrease of the concentration of their active hydroxyl end-groups with increasing the molecular weight of PEGs.

However, the extent of polymerization – reactions (p), calculated from Carothers equation $\overline{DP}_n = 1/(1-p)$, for PU106 to PU4000 (Table 1) showed a linear relationship (unlike that of $\overline{DP}_n$) decreasing with increasing the molecular weights of their PEGs.

Attempts to increase the extent of polymerization for PUs of high molecular weight of PEGs were attempted. For example, a homogeneous solution polymerization, analogous to a reported for MDI with ethylene glycol [16] was carried out by the addition of a solution of PEG2000 (20 g) in dried dimethylsulfoxide (30 ml) into a stirred suspension of MDI (2.5 g) in MP (20 ml). The reaction was heated (130°C, 6 hours) and then PU2000 (m.p. 51-53°C) was received as previously. This showed a somewhat higher reduced viscosity (0.27dl·g^{-1}, c = 0.5%) than that (0.21dl·g^{-1}, [n] = 0.20 dl·g^{-}1) of PU2000, which was prepared using as polymerization solvent only MP under somewhat milder reaction conditions (115°C, 5 hours).

In connection to the above procedure, it must be noted that polar basic solvents with free electron pairs were avoided to be used as direct solvents of MDI, because analogous compounds (*tert*-amines, -amides, -phosphines, phospholines, etc.) may catalyze self-condensation/polymerization of isocyanates [17-19].

Furthermore, melt polymerization of equimolar also quantities of MDI and PEG2000 (130°C, 2 hours) under nitrogen stream provided PU2000 with a reduced viscosity value (0.16dl·g^{-1}, c = 0.5%) similar to that of PU2000 prepared in MP (Table 1).

Conclusively, the attempted alternative procedures with high molecular weight PEGs (PEG2000) to provide PUs of high polymerization degree were also ineffective.

CONCLUSION

Elemental analysis and I.R. spectra of the prepared polyurethanes PUs106 – PU4000 were consistent with their structure (I). PU106 derived from diethylene glycol (MW: 106.12) showed the maximum T_m, T_g, [n], $\overline{M}_n$, and $\overline{DP}_n$, while PU200 and PU400 where amorphous. PU1000, PU2000, and PU4000 showed low DP_n values (9, 6 and 3, respectively), as a result of the presence as well of an amount of low molecular weight derivatives (low oligomers), as showed TLC tests. This reduced reactivity was attributed to the decrease of the concentration of reactive end-groups with increasing the molecular weight of the PEGs. I.R. spectra showed that the urethane imide groups were highly bonded (approx. 94%) in PU106 and PU200, mostly bonded in PU4000–PU2000 and less bonded (approx. 43%) in PU4000. T_g, [n] and $\overline{DP}_n$ values of PU106–PU4000 vs. their PEG molec-

ular weights showed relationship curves with an initial deep fall following then a slight reduction. However, the extent of polymerization values showed a linear relationship, respectively.

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