

Bromine – containing polyurethane ionomers

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Summary

Polyurethane ionomers with reduced flammability were obtained by incorporating a brominated chain extender (dibromoneophenyl glycol - DBNPG) into the ionomers based on isophoronediiisocyanate, polyoxytetramethylene glycol and 2,2-bis(hydroxymethyl)propionic acid. To examine the influence of brominated diol on the characteristics of the synthesized polymers, model polyurethane compounds containing various amounts of brominated and nonbrominated chain extenders (1,4-butanediol and neopentyl glycol) were prepared, as well. The products were studied by FTIR, DSC and TGA methods. Hydrolytic stability of the ionomers in water was controlled by FTIR; their flammability was examined by oxygen index measurements.

Introduction

It is known that halogen ingredients contribute to the flame resistant properties of polymers (1,2). Bromine and chlorine are generally regarded to act primarily as flame retardants during combustion by interfering with the flame propagation in the vapour phase. Bromine and phosphorus additives are usually used to suppress the combustion of polyesters, as well as of flexible polyurethane foams (3-5). Brominated diols were found to be very efficient flame retardants allowing easy processing and preparation of a wide range of polyurethane formulations. Therefore they still can not be adequately replaced with some alternative, less health hazardous systems. From that point of view it is very important to determine the minimal amount of bromine ingredients to obtain a reduced flammability.

A survey of literature revealed that polyurethanes based on halogenated monomers were often hydrolytically unstable (6,7). However, Yang et al. (8) used fluorine containing polyol in preparation of stable anionic aqueous polyurethanes.

The present study is a part of the project concerning the synthesis, characterization and application of polyurethane ionomers (9-11). It was undertaken to examine the suitability of using the brominated diol DBNPG in the preparation of flame resistant and hydrolytically stable polyurethane ionomers. DBNPG was chosen because it did not contain hydrogen atoms on the carbon atom adjacent to bromine containing carbon

atom, thus providing a resistance to dehydrobromination by chemical reaction or by photodegradation. According to Miller (12) the hydrolysis of DBNPG in water is slow with a rate constant of about 10^{-5}sec^{-1} at 100°C .

This work presents the study of structural features of the polyurethanes prepared with brominated and nonbrominated chain extenders, and the investigation of flammability and hydrolytic behaviour of the ionomers synthesized thereof.

Experimental

Materials

Isophorone diisocyanate (IPDI, Fluka), polyoxytetramethylene glycol of molar mass 2000 g/mol (PTMO 2000, BASF), 1,4-butanediol (BD, Aldrich), neopentyl glycol (NPG, Fluka), dibromoneopentyl glycol (DBNPG, D.S. Bromine Company LTD), 2,2-bis(hydroxymethyl)propionic acid (DMPA, Aldrich), triethylamine (TEA, Merck), solvent tetrahydrofuran (THF, Merck) and catalyst dibutyltin dilaurat (DBTDL with 18% tin content, Acima) were used. PTMO 2000 was degassed under vacuum by heating it at 70°C for 8h; BD and THF were dried by storing them over 4\AA molecular sieves.

Synthesis

Model compounds of various composition (Table 1) were synthesized from the prepolymer based on PTMO 2000 and IPDI and different types and quantities of chain extenders (BD, NPG, DBNPG).

Table 1: Composition of model polyurethane compounds

Sample	Moles of reactants					Mol. % of hard segm. ^a	Wt. % of Br ^a
	PTMO 2000	IPDI	DBNPG	BD	NPG		
PUDBNPG1	1	2	1	-	-	75.0	5.9
PUDBNPG3	1	4	3	-	-	87.5	13.1
PUDBNPG5	1	6	5	-	-	91.6	17.1
PUNPG5	1	6	-	-	5	91.6	-
PUBD1	1	2	-	1	-	75.0	-
PUBD5	1	6	-	5	-	91.6	-

^a Calculated data

Ionomers were synthesized from PTMO 2000, IPDI, DMPA (neutralized by an equivalent amount of TEA) and BD, which was gradually replaced by the brominated compound DBNPG, keeping the molar shares of the hard segments, NCO/OH, and of DMPA/polyols constant (Table 2). The properties of the products were, therefore, influenced by the bromine content only.

Model compounds were synthesized in 40% THF solutions at 80°C, while ionomers at 60°C with 0.2 wt% of DBTDL catalyst.

Table 2: Composition of polyurethane ionomers

Sample	Moles of reactants					Mol. % of hard segm. ^a	Wt. % of Br ^a
	PTMO 2000	IPDI	DBNPG	BD	DMPA		
A	1	7	-	4	2	92.8	-
B	1	7	1	3	2	92.8	3.5
C	1	7	3	1	2	92.8	9.8
D	1	7	4	-	2	92.8	12.6

^a Calculated data

Methods

IR spectra were recorded on a Perkin Elmer spectrometer FTIR 1725X. The samples were prepared by casting their THF solutions onto NaCl plates.

Glass transition temperatures (T_g) and melting temperatures (T_m) were measured by differential scanning calorimeter Perkin Elmer DSC-7. The dried samples were heated with a rate of 10°C/min.

Thermogravimetric measurements were performed on a TA 2000 instrument (TA Inst. Inc. USA). The samples were heated up to 600°C with a rate of 10°C/min in the air.

Flammability was determined by measuring the oxygen index (OI) using a Stanton Redcroft instrument according to ASTM D 2863-77 standard.

The courses of reactions between diisocyanate and glycols were followed by titration of unreacted NCO groups.

Results and discussion

The experimental conditions for the synthesis of model compounds and ionomers (temperature, time, amount of catalyst) were selected on the basis of our preliminary study of the reaction rates between IPDI and different glycols in THF solution. It was

found out that the reaction of IPDI with DBNPG was slower than the reactions with BD and NPG. Similar behaviour has been observed in some chlorinated and fluorinated polyurethanes (13). The lower reactivity of DBNPG was attributed to the steric hindrances due to its branched structure, and to the interactions in solution caused by dipole moments as well as by hydrogen bonding.

Characterization of model compounds

FTIR analysis

Polyurethane properties depend on the segmented structure, on the extent of phase mixing, as well as on secondary bonds, e.g. hydrogen bonds. By using IR spectroscopy hydrogen bonding between C=O and N-H groups of model compounds was studied.

The influence of various chain extenders onto hydrogen bonding is evident from Figure 1. The absorption band of C=O stretching vibrations is in all samples wide and nonresolved which means that the absorption bands of hydrogen-bonded and nonbonded (free) C=O groups overlap. This is characteristic of the poorly phase segregated polyurethanes. However, the C=O band is shifted to different frequencies: to 1718 cm^{-1} in PUDBNPG5, to 1709 cm^{-1} in PUNPG5, and to 1700 cm^{-1} in PUBD5. The magnitude of C=O and N-H frequency shift is a measure of the hydrogen-bond strength. Therefore, it has been assumed that the hydrogen bonds of brominated compound are the weakest. The changes in the N-H vibrations range confirm this assumption because the ratio of the absorption bands of the free N-H groups at 3426 cm^{-1} to the bonded N-H groups at 3327 cm^{-1} is the highest for PUDBNPG5. Similar shift trend has been also observed in the tetrafluorobutanediol chain-extended polyu-

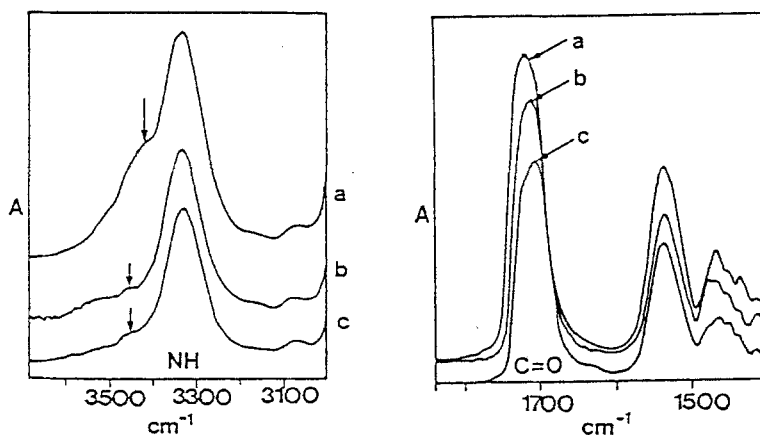


Figure 1: FTIR spectra of the N-H and C=O absorption regions of model compounds: a) PUDBNPG5, b) PUNPG5, c) PUBD5

rethanes when compared to the butanediol chain-extended polyurethanes (14).

Our results show that the branched structure as well as the presence of bromine in the polymer chain cause weakening of hydrogen-bonds, and as a consequence, an enhanced phase mixing can be expected. However, the differences in hydrogen-bond strength of the examined samples are too small to influence the mechanical properties of the polymer films.

DSC analysis

Thermal behaviour of the model compounds was investigated by measuring T_m and T_g transitions in the range from -100 to 200°C. The enthalpy of melting (ΔH) of the soft segments and the specific heat (Δc_p) at T_g were calculated as well (Table 3).

In DSC curves of PUBD1 and PUDBNPG1 distinctive melting peaks of the soft segments were found. In these samples the molar share of soft segments was the highest. T_m peak of the soft segments in PUDBNPG3 was broad, while T_m peak of PUDBNPG5 was very small and hardly observable. Melting peaks of the hard segments were not found in the examined temperature region. Table 3 shows that the enthalpy of soft segments decreases with the increase of bromine content. Besides, the enthalpy of PUDBNPG5 is lower than the enthalpy of PUNPG5 and PUBD5 although they all have the same amount of soft and hard segments. This indicates some enhanced phase mixing in the brominated compound.

Table 3: Thermal transitions of model compounds

Sample	T_m (°C)	ΔH (J/g) ^a	T_g (°C)	T_g (°C)	Δc_p (J/g°C) ^a	Δc_p (J/g°C) ^a
	soft segm.	soft segm.	soft segm.	hard segm.	soft segm.	hard segm.
PUDBNPG1	24.8	72.1	-69.9	-	0.46	-
PUDBNPG3	26.3	65.5	-37.7	-	0.77	-
PUDBNPG5	27.1	4.2	-10.8	-	1.07	-
PUNPG5	25.3	70.2	-67.4	40	0.44	0.57
PUBD1	29.0	88.7	-79.2	-	0.40	-
PUBD5	28.2	69.8	-72.3	30	0.52	0.62

^a Calculated per weight fraction of the soft and hard segments.

Compounds without or with a small amount of bromine have T_g of soft segments in the range from -79.2 to -67.4°C, while PUBD5 and PUNPG5 with a higher amount of hard segments have transitions at 30 and 40°C corresponding to T_g of the hard seg-

ments. The noticeable increase in T_g of soft segments (from -69.9 to -10.8°C) with the increase of bromine amount (PUDBNPG1, PUDBNPG3, PUDBNPG5) suggested enhanced phase mixing again. This was confirmed by the simultaneous increase of the specific heat at T_g . However, the additional dipole-dipole interactions in the brominated compounds may have an influence on T_g at the same time. The conclusions based upon the DSC results are consistent with the FTIR results as well as with the literature data (14).

TGA analysis

By using thermogravimetry, thermal stability of the samples having equal soft and hard segments ratio, but different chain extenders, was examined.

Thermal degradation of the branched PUNPG5 starts at the lowest temperature ($T_{\text{onset}} = 266^\circ\text{C}$), of the linear PUBD5 at 280°C and of PUDBNPG5, which is branched and contains bromine, at 298°C . TGA curves of nonbrominated PUNPG5 and of brominated PUBDNPG5 are presented in Figure 2.

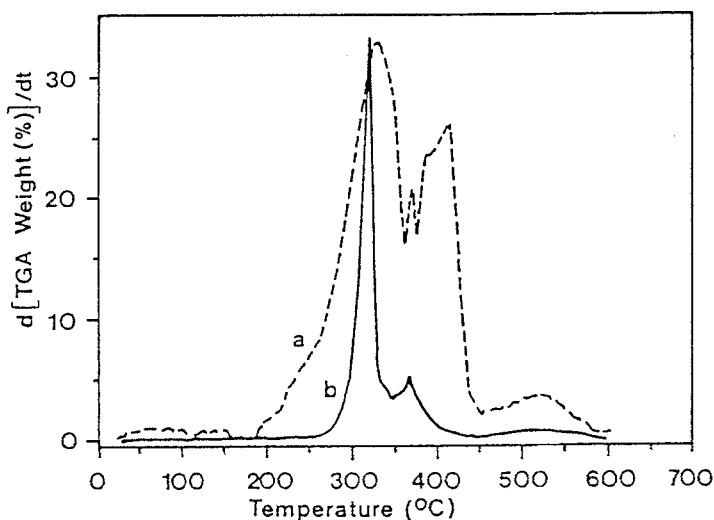


Figure 2: Thermal degradation in air of: a) PUNPG5, b) PUDBNPG5

The highest value of the onset of PUDBNPG5 thermal degradation shows that the presence of bromine in the polymer slightly increases its thermal stability.

Characterization of polyurethane ionomers

Samples of polyurethane ionomers A, B, C and D (see Table 2) were characterized by FTIR, DSC and TGA. The results were in good agreement with the data obtained for model compounds. The particular interest in ionomers was focused on their stabili-

ty in water and on their flame resistance.

Hydrolytic stability

With the same amount of ionic groups, ionomers A and B formed a dispersion when mixed with water, while ionomers C and D, having a higher bromine content, formed a colloidal solution. This was explained by the increased polarity of higher brominated polymers.

The stability of water dispersions and solutions was controlled for three months. In that period of time precipitation or other visible changes were not observed. Hydrolytic stability was followed by scanning FTIR spectra of the films from ionomers before and after mixing with water and of films from water dispersions and solutions cast every two weeks during the three months period. According to Miller (12), the mechanism of hydrolysis of DBNPG appears to involve the loss of bromine with the concurrent formation of an oxetanium ion. The reaction of this ion with water then yields the triol. However, in the spectra of tested films no changes were observed which led to an assumption that brominated ionomers were hydrolytically stable. The size exclusion chromatography measurements showed that molar masses and molar mass distributions of the investigated films did not change, which confirmed the assumption of the hydrolytic stability of the synthesized ionomers.

Flammability tests

Although the oxygen index method does not give results which correlate with flammability data produced from "real fire" scenarios (15,16), it is widely used to evaluate the influence of additives or some other ingredients on polymer flammability.

The oxygen index (OI) values of the ionomers point out that flammability of the films is a function of the bromine content (Table 4). By experimental work with different polymeric materials the limiting value of OI has been accepted to be 28% (materials having OI > 28% did not burn in the air). According to this value, all synthesized brominated ionomers can be regarded as nonflammable.

Table 4: Oxygen index of ionomers films

Sample	Wt. % of Br	Oxygen index (%)
A	without Br	23.3
B	3.51	29.5
C	9.78	31.8
D	12.60	32.6

Conclusions

Due to the branched structure and to the presence of bromine, dibromoneopentyl glycol changed some characteristics of polyurethane ionomers when incorporated into the polymer backbone; bromine influenced the hydrogen-bonds strength in a small extent, but it significantly increased the T_g values. The increase of T_g of the brominated compounds was ascribed to the stronger dipole-dipole interactions and enhanced phase mixing. Due to a higher polarity the more brominated ionomers formed colloidal solutions. Water dispersions and solutions of brominated ionomers were hydrolytically stable. DBNPG slightly increased the thermal stability of polyurethane ionomers, while 3.5 wt% of Br were found to be sufficient to reduce their flammability.

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