

PREPARATION, PHYSICAL PROPERTIES AND MODEL ANALYSIS OF LINEAR HOMOGENEOUS POLYURETHANE

M.LAPORTA, M.PEGORARO, F.BIANCHI, DEPT. OF CHEMISTRY, MATERIALS, CHEMICAL ENGINEERING GIULIO NATTA; G.CONSOGLATI, INFIM DEPT. OF PHYSICS- POLITECNICO OF MILAN- Piazza Leonardo da Vinci 32, 20133 Milano, Italy
L. ZANDERIGHI; DEPT. OF PHYSICAL CHEMISTRY, UNIVERSITY OF MILAN
Via Golgi 19, 20133 Milano, Italy

ABSTRACT

PU block polymers are constituted by sequences of constitutional units CU which are : a diisocyanate T, a polyol or a polyamine V, an extensor E. Due to the CU different solubility parameters, hard and soft micro domains are formed; they can aggregate into different phases. A linear PU can be described by two parameters $R=T/V$ and $R_E=(R-1)V/E$. A stoichiometric model is proposed which gives the general formula of all the possible PU: $X((TV)_k(TE)_n)_mX$, where k and m can be calculated from the experimental molecular weights respectively of pre polymer and polymer and $n= R-1$. Physical properties depend on PU composition and on nature of CU. I.R. analysis is useful for discovering the hydrogen bonds location; DSC gives informations on the presence of the different phases. PALS analysis shows that nano cavities become tighter on increasing n. A series of particular PUs, obtained from TDI, a low molecular weight polyol, a cyclic extensor, at different R and R_E was prepared and analysed. These PU are amorphous, monophasic and appear to be good candidates for membranes.

INTRODUCTION

Linear polyurethanes are block polymers constituted by an alternating sequence of molecules defined constitutional units (CU), whose physico-chemical characteristics determine either the stiffness or the flexibility of the blocks. A sequence of stiff blocks is usually called hard segment while a sequence of flexible blocks is called soft segment. The hard and the soft segments may interact by forming an homogeneous phase, or may segregate into a two phase system. When the segregated hard segments are dispersed into a continuous soft phase, they may aggregate forming a short range order phase known as domains or lamellae. Usually three type of CUs are present in linear PU: a diisocyanate (T), a long chain glycol, such for instance a polyether or a polyester diol of high molecular weight (V), and a glycol or a diammine, of low molecular weight, known as extensor (E). T and E react with formation of stiff blocks, while T and V originate flexible blocks; more the length of V more the flexibility of the block. Usually high molecular weight (>1000) are used in elastomeric PU. In this paper we have studied how to obtain monophasic amorphous PU with the aim to get membranes with a very high permeability, since hard domains inhibits the permeability.

EXPERIMENTAL.

Preparation: a short chain polyetherdiol ($M_n=431$ dalton), a mixture (80/20 %) of 2-4 and 2-6 toluene diisocyanate and an extender (E) such, as 1-4 cyclohexane dimethanol, with different ratios: $R=T/V$ (1.3; 1.5; 1.7; 1.9; 2.1; 2.5; 2.8; 3.3) and $R_E=(T-V)/E$ (0.5; 1; $1/(R-1)$) have been used.

DSC: in table 1 the glass transition temperature T_g , the ΔC_p across glass transition of the prepared PU, of pure [V] and of the $[TE]_n$ polymer are reported. The presence of only one T_g suggest that the material is an homogeneous homophasic system. In the last column of the table the hard blocks weight fraction evaluated according to the relation:

$$X_H^w = (w_T + w_E) / (w_T + w_E + w_V)$$

as defined in the literature, is reported.

The T_g values of the studied PUs are in the range 303-362K. This wide range variation indicates that the introduction of [V] in the $[TE]_n$ polymer first of all eliminates the phase segregation, since only one T_g is present in PUs, moreover by increasing the amount of [T] in the PU's, the T_g s increase from a temperature lower than that of the first T_g of pure $[TE]_n$ until a value higher than the second T_g temperature of pure $[TE]_n$.

IR: the bands have been analysed in frequency, height, width at half height and area, or in the second derivative to solve the broad bands in their component peaks. The relative absorbance of C=C (1414 cm^{-1}) and C=O ($1751\text{-}1717\text{ cm}^{-1}$), in agreement with stoichiometry, increase by

increasing R. A similar behaviour has been observed for the band of $\gamma(\text{O-C=O})$ at 769 cm^{-1} . The ratio between the normalised bands C=O ($1717\text{-}1665\text{ cm}^{-1}$) and C=C ($1430\text{-}1390\text{ cm}^{-1}$) results independent from R. The normalized area in the region $1176\text{-}1028\text{ cm}^{-1}$, typical of hard segments (T-E) O-C=O stretching and of the ether group O-C-O , reveals an increase of the total amount of the oxygen is observed on increasing R.

Table 1
Glass transition temperature and Δc_p transition values for the various polymers. In the last column the weight fraction of hard segment x_H is reported.

R	T_g (K)			Δc_p (J/g K)			x_H^w
	1/1	1/2	1/(R-1)	1/1	1/2	1/(R-1)	
1.3	308	303	308	0.39	--	0.35	0.34
1.5	315	315	315	0.30	0.38	0.27	0.38
1.7	315	323	314	0.33	0.33	0.39	0.41
1.9	320	332	315	0.47	0.39	0.40	0.43
2.1	339	321	334	0.22	0.34	0.28	0.46
2.5	334	342	335	--	0.36	0.30	0.50
2.8	355	348	339	0.26	0.34	0.34	0.53
3.3	362	350	337	--	0.29	0.27	0.57
	T_g (K)			Δc_p (J/g K)			
[V]	200			0.60			
[TE] _n	306			0.28			
	350			0.32			

From the composition it results that the number of NH groups present are equal to the C=O groups, since they derive from the same molecules [T], while the number of C-O-C groups, in polyol, are 7-8 times the NH groups. This means that for each NH group there are about 8-9 oxygen groups available for hydrogen bonding. From the values of the integrated area of free (3343 cm^{-1}) and bounded (3304 cm^{-1}) N-H it is possible to evaluate the N-H fraction involved in hydrogen bonds. By using this procedure it results that more than 98% of N-H groups are involved in hydrogen bond for all PU samples.

Other useful sources of information on hydrogen bond are the urethan (C=O) band region $1751\text{-}1651\text{ cm}^{-1}$, the (O-C=O) carboxy groups in the region $1060\text{-}1035\text{ cm}^{-1}$, the polyether (C-O-C) band at 1093 cm^{-1} .

The IR analysis indicates that:

- hydrogen bonds increase with R;
- a large fraction of NH groups are hydrogen bonded with the oxygen present in ether group;
- by increasing R the fraction of NH hydrogen bonded to C=O groups increases with respect to that one bounded to C-O-C groups.
- No evidence of a biphasic system, such as hard or soft domains, has been observed; a suggestion of an homogeneous system is the most acceptable.

PALS: only some samples, representative of all prepared PU, have been studied by *PALS*, since we preferred to investigate the effect of temperature in a temperature range around the T_g to investigate if the glass to rubber transition introduce significant variation on the free volume. The obtained data are reported in table 2. For each sample only one o-Ps lifetime τ_3 was detected, indicating that only one modal distribution of free volumes is present. A comparison between the intensity I_3 indicates that the formation probability of Ps doesn't change by increasing the temperature across T_g , and does not show significant variations among the various samples. The mean hole volume $\langle V \rangle$ has been evaluated from annihilation lifetime τ_3 and is shown in table 2 together with the width σ_V of the volume distribution. for each value also the hole distribution σ_V and the χ value of the chi tests has been calculated. For the investigated PU samples a systematic increase of the mean hole volume with temperature is observed which can be expected, since the chain movements are no longer "frozen in" above T_g [TE]_n has $\langle V \rangle$ value lower than PU polymer; this suggests that the

introduction of soft segments in the [TE]_n structure increase the free volume, probably owing a decrease in hydrogen bond strength and an increase of the mobility of polymer chain. As a general conclusion it is possible to say that the free volume increases with temperature are similar for the various samples; moreover the presence of only one lifetime o-Ps distribution support the hypothesis of a monophasic system.

Table 2

Annihilation time τ_3 (ns) and intensity(%) of PAS for some PU samples.

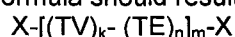
Sample	Temp(K)	τ_3 (ns)	I_3 (%)	$\langle V \rangle$ (Å ³)	σ_V (Å ³)	χ^2
1,3(1:1)	297	1.94	23.4	84.7	32.8	0.99
	320	2.16	21.9	109.1	27.0	1.03
3,3(1:1)	297	1.85	22.6	71.8	40.6	1.02
	344	1.98	21.9	90.3	28.8	1.06
	375	2.23	22.7	105.3	54.3	1.06
1,3(1:2)	297	1.91	20.7	81.8	32.8	1.00
	318	2.09	20.2	99.0	36.4	1.03
3,3(1:2)	334	2.23	21.0	116.0	26.0	1.07
	365	2.52	20.8	139.7	48.8	1.01
T-E	312	1.65	22.1	61.8	22.0	1.01
	343	1.94	21.2	88.1	25.7	1.01

DISCUSSION

A stoichiometric model to evaluate the domains present in PU, is presented here, which has the advantage of simplicity and of a good correspondence to the Pu structure.

Prepolymer. If it were possible to prepare the prepolymer molecules one at a time, (mono-dispersed polymer) each molecule could be represented by formula [TV]_kT, with k changing according the reaction stoichiometry. By defining $R = [T]^0/[V]^0$, we get for [TV]_kT, $R = (k+1)/k$, that is: $k = 1/(R-1)$; k is decreasing from ∞ (for R=1), to 1 for R=2. For R>2, T cannot be added to TVT anymore and the reaction product is a mixture of the oligomer [TVT] and of unreacted [T].

PU. In the second step the pre-polymer is reacted with the extensor E, which is a low molecular weight substance; hydroxyl or amine terminated. Usually a bifunctional [E] is used in linear PU preparation; when [E] is polyfunctional [7], a cross-linked PU is obtained. Let us assume to react, ideally and separately, n molecules of [E] with the free [T], if any, and one molecule of [E] with one of [TV]_kT, and to mix the reaction product in order to obtain the final PU product the following general PU formula should result:



where X represent the reactant present in excess in the second stage, that is [E] or [TVT]. k and n can be obtained from the value of R and R_E, m from the experimental molecular weight of the PU. The values of k, n, m for the synthesized PU are reported in table 3:

Table 3

Values of the parameter m and n evaluated according to stoichiometric model from experimental molecular weight

R	N	Re = 1	Re = 0,5	Re=1/(R-1)
		M	m	M
1.3	1	20.2	25.2	22.5
1.5	1	32.9	28.7	35.9
1.7	1	39.6	24.8	42.8
1.9	1	44.4	64.6	43.7
2,1	1.1	45.3	8.5	54.7
2.5	1.5	47.5	36.1	37.8
2.8	1.8	29.1	42.7	42.5
3.3	2.3	6.1	37.7	9.4

k, n, m are statistically distributed around mean values; with the proposed model it is possible to determine their numeral mean values on the basis of the PU composition and mean numeral molecular weight.

The proposed stoichiometric model is based on the following considerations:

- the pre polymer composition depends only on one parameter k, which can be easily determined either from stoichiometry of the reaction or from the analysis of its equivalent weight;
- parameter n depends on R and R_E. It is equal to the number of the TE (hard) groups per molecule of PU.
- for known values of the parameters k and n the formula of the basic building blocks can be easily written; the parameter m can be calculated from the experimental PU molecular weight.

A new definition of hard and soft blocks fraction x_H^n based on block fraction evaluated from the k and n values, according to the equation: $x_H^n = n/(k+n)$, where x_H is the hard segment fraction can be introduced. For comparison the x_H^w and x_H^n values are reported in table .

Table 4
Weight fractions(x_H^w) and segment fraction(x_H^n) of hard domains in the studied PU.

R	x_H^w	x_H^n
1.3	0.39	0.23
1.5	0.44	0.33
1.7	0.48	0.41
1.9	0.52	0.47
2.1	0.55	0.52
2.5	0.60	0.60
2.8	0.63	0.64
3.3	0.68	0.70

Since the prepared PUs are monophasic block copolymer of (TV)_k and (TE)_n and that the empirical Fox Flory equation used in correlating the T_g data of various PU with x_H^w , is not successful, a new empirical equation is proposed, that use the polymer block fraction x_H^n , for evaluating the glass transition temperature, T_s and T_H, respectively of the soft and of the hard blocks:

$$\frac{1}{T_g} = \frac{x_H^n}{T_H} + \frac{(1-x_H^n)}{T_s}$$

Moreover a linear relationship between the T_g values and the segment fraction x_H^n has been tested:

$$T_g = x_H^n T_H + (1-x_H^n) T_s$$

Also in this case mean T_gs over the three set of data have been considered. The obtained values of T_s and T_H are reported in table 5.

Table 5
Calculated T_g values (K) for the soft and the hard segments.

PU	Equation Fox Flory				Equation linear			
	1/1	1/2	1/(R-1)	mean	1/1	1/2	1/(R-1)	mean
T _g (soft)	289±16	293±26	297±25	293±14	284±7	289±5	295±5	289±2
T _g (hard)	375±20	367±26	351±25	364±15	371±8	363±6	349±6	352±3

CONCLUSION

We have found that the phase separation cannot occurs in PU when they are prepared with CU of low molecular weight and in a suitable stoichiometric ratio. The monophasic amorphous PUs are of great interest for the preparation of high permeability membranes as shown by us in many cases, mainly for water vapour separation.

The simple stoichiometric model presented in this paper may be useful for getting information on the structure of any PU and on control the structure of new PU.