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NEW AROMATIC POLY(AZOMETHINE URETHANES)

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ABSTRACT

New poly(azomethine urethanes) (PAMU) with linear structures were prepared in the conventional literature manner by reacting 4,4'-methylene bis(4-hydroxybenzylideneaniline) and 4,4'-methylene bis(2-hydroxybenzylideneaniline) as azomethine bisphenols, with various diisocyanates such as 4,4'-methylene bis(4-isocynato-phenyl) (MDI), 2,4-toluylene diisocyanate (2,4-TDI) and 1,6-diisocyanatohexane (HMDI). The resulting polymers were first confirmed by IR, ^{1}H-NMR spectra and elemental analysis, then characterized by viscosity, solubility, thermo-gravimetric analysis (TGA) and UV measurements. A semicrystalline behavior was noticed for some polymers by X-ray diffraction and differential scanning calorimetry (DSC) measurements.

INTRODUCTION

Polyazomethines (PAM) are an important class of thermotropic polymers that have potential as high performance fibers [1]. Also, PAM are of great interest because of their high thermal stability in forming chelates, and for semiconducting properties [2]. There is some literature concerning poly(azomethine urethanes)

(PAMU) [3-5]. Our paper presents the synthesis and characterization of some new linear PAMU obtained from aromatic or aliphatic diisocyanates, and para-/ortho-linked azomethine bisphenols.

EXPERIMENTAL

Materials

4,4'-Methylene-di(phenyldiisocyanate) (MDI, I), 2,4-toluylene diisocyanate (2,4-TDI, III) and hexamethylene diisocyanate (HMDI, IV) all from Fluka, were purified by distillation under reduced pressure. Dimethylformamide (DMF, Merck) and 1-methyl-2-pyrrolidinone (NMP, Merck) were purified by distillation over phosphorus pentoxide prior to use.

Techniques

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena spectrophotometer by using the KBr pellet technique. ^{1}H-NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 80°C in DMSO-d_6 as the solvent, using TMS as the internal reference. Polymer solubilities were made for 8 common solvents at a concentration of 1% (w/v) at room temperature. Differential scanning calorimetry (DSC) measurements were done with a Mettler TA Instrument DSC 12E at a heating rate of 10°C/min, in nitrogen. The X-ray diffractograms were recorded using a TUR-M62 apparatus and nickel-filtered CuKα radiations.

Synthesis of Monomers (IIa,b) and Polymers (V-VII a, b)

Both azomethine monomers (II a, b) were prepared and purified as described elsewhere [6]. All the polymers were synthesized and purified as described in a previous paper [4]. A typical example for the synthesis of polymers follows. To a solution of 4.065 g (0.001 mol) bisphenol IIa in 25 mL DMF, were added 0.2753 g (0.0011 mol) I in 25 mL DMF at 60 °C during 1 hour. The temperature increased at 140°C and the reaction mixture was stirred under nitrogen for 5 hours and left over-night for the completion of the reaction. The PAMU V-VIIa,b thus prepared were precipitated with distilled water, filtered off, washed several times: first with water, then with methanol, and dried for 48 hours in a vacuum oven at 60°C. The properties of the PAMU V-VIIa,b are presented in Table 1.

TABLE 1. The Properties of Polymers V-VII a, b

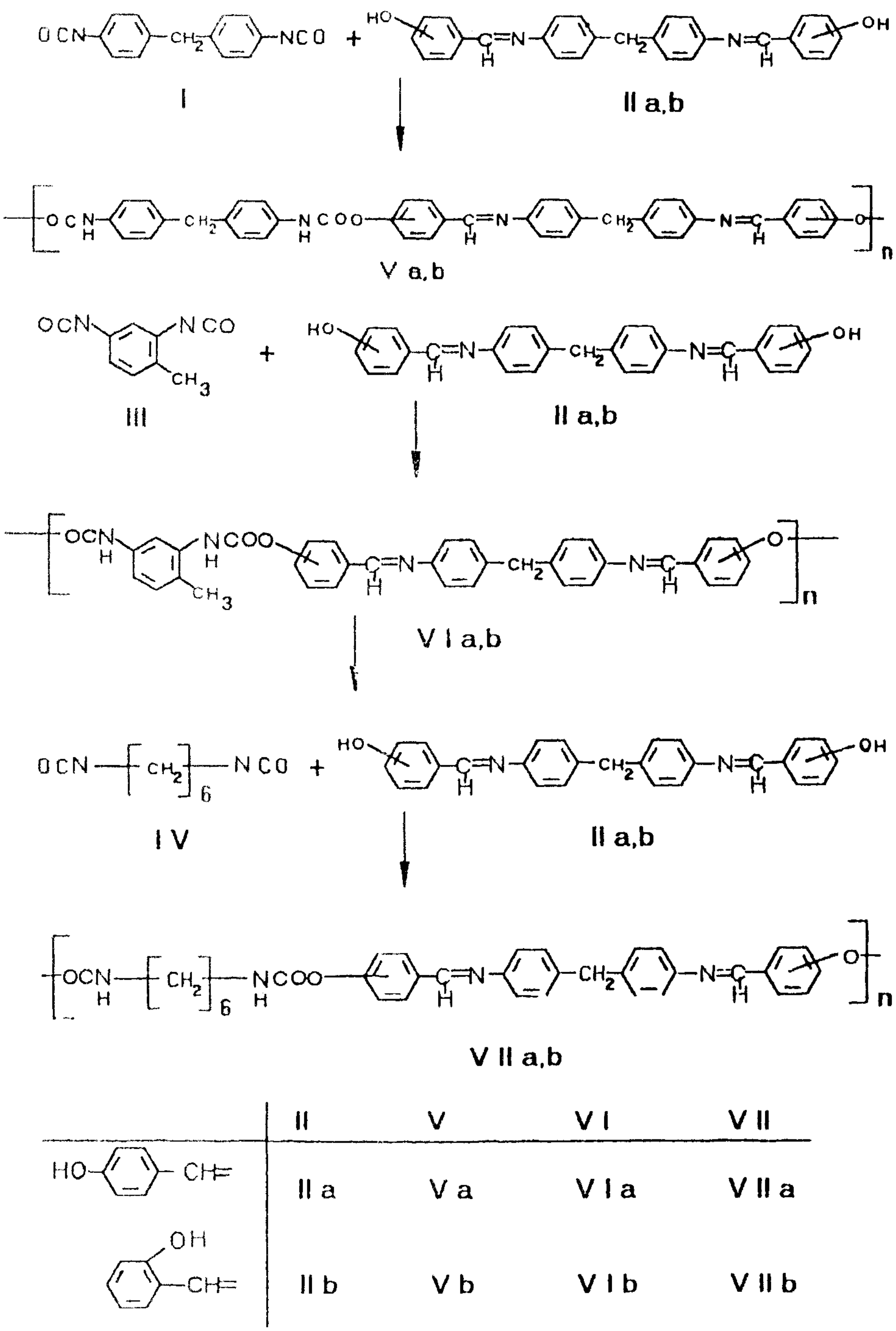
Polymer	Yield, %	Melting range, °C	Reduced viscosity[a], dL/g	Thermal Properties, °C T_{10}[b]	TOA[c]	DSC[d]
V a	90	225-230	0.32	330	228	230
VI a	91	238-245	0.10	345	238	247
VII a	95	206-210	0.29	313	241	247
V b	83	203-210	0.28	325	219	210
VI b	80	203-209	0.31	340	210	216
VII b	89	188-194	0.32	303	225	221

[a]Measured in NMP at a concentration of 0.2 g/dL at 25(±0.1°C; [b]TGA temperature for 10% weight loss; [c]TOA measurements in air; [d]DSC measurements, first heating cycle in nitrogen.

RESULTS AND DISCUSSION

PAMU (V-VII a, b) were prepared by the reaction of the bisphenols II a, b with various diisocyanates (I, III, IV), as shown in Scheme 1. The structures of the polymers were confirmed by IR, ^{1}H-NMR spectra, and elemental analysis data. IR spectra of PAMU showed characteristic absorption bands in the 1720-1690 cm^{-1} range due to the carbonyl groups in the urethane moiety, and in the 3340-3320 cm^{-1} range due to the N-H stretching, in addition to other absorption bands representative for the aromatic, aliphatic and azomethine groups. As a typical example, the ^{1}H-NMR spectra of the polymers V b and VI b (Figure 1) showed the two characteristic peaks (singlets) centered at 8.925, 8.375 (V b) and 9.0, 8.45 ppm, (VI b) assigned to -NH-COO- and -CH=N- protons, respectively.

Also, the singlets centered at 4.0 ppm, assigned to the -CH$_2$- protons, are present along with the peaks in the 7.8-7.0 range assigned to other aromatic protons. The reduced viscosity values of polymers V-VII a, b (Table 1), ranged between 0.10 and 0.32 dL/g, and were at least close to those reported for similar PAMU [4, 5].


I
II a,b
V a,b
III
II a,b
VI a,b
IV
II a,b
VII a,b
II
V
VI
VII
II a
V a
VI a
VII a
II b
V b
VI b
VII b

SCHEME 1

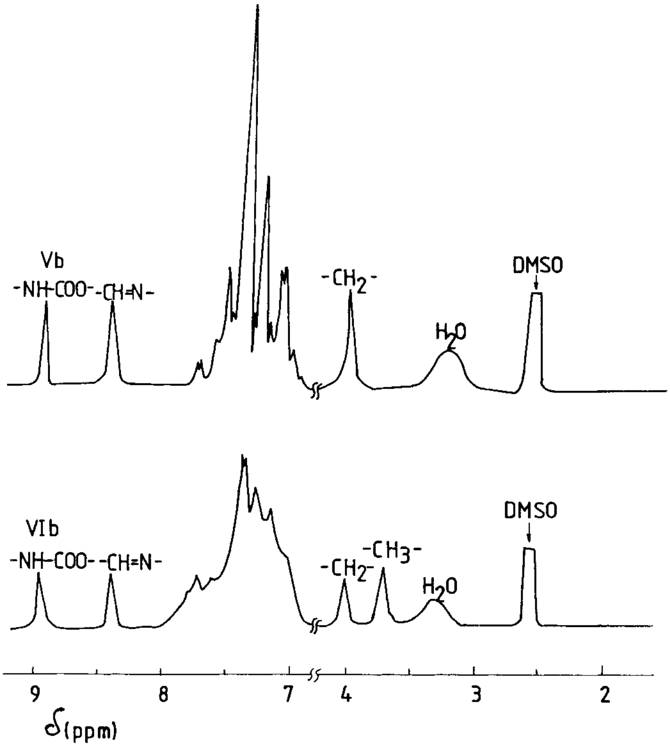


Figure 1. ^{1}H-NMR spectra of polymers V b and VI b.

X-ray diffraction curves showed that the reported PAMU exhibited crystalline behavior [3, 5]. Our PAMU (V-VIIa,b) exhibited melting behavior (Table 1), confirmed by TOA and DSC measurements. The polymers melted in the 188-245°C range. As can be seen, the PAMU Va-VIIa melted at higher temperature than their corresponding ortho- analogs (V b-VII b); a similar behavior was observed for linear polyesterazomethines [2]. It was also noticed that 1,6-hexamethylene flexible chains, in the polymer backbone, lowered the melting temperatures [2,7]. The TOA curves for all the polymers indicated a single change in the variation of the transmited light intensity, and the corresponding values of the temperature for this change agree reasonably well with the DSC ones. The absence of other previous transitions (i.e., glass transition) permitted us to consider the sharp endotherms from DSC thermogram as melting temperatures of polymers; thus supporting the crystalline morphology of the polymers [8].

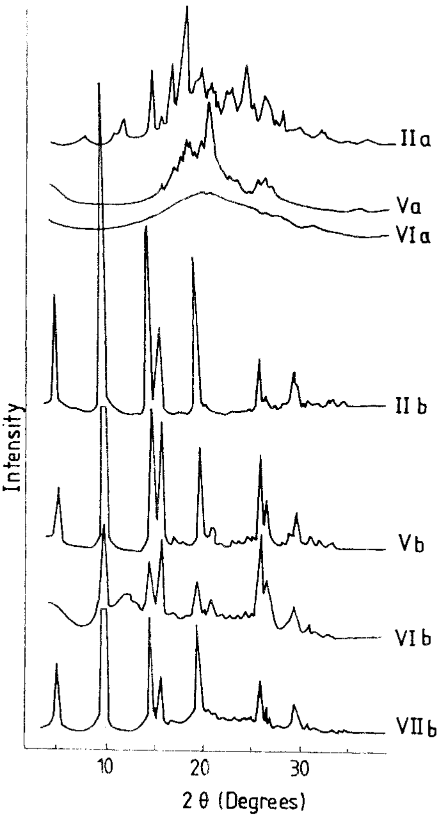


Figure 2. Wide angle X-ray diffraction scans of monomers II a, b and polymers V a, VI a, V-VII b.

TABLE 2. The Solubility of Polymers V-VII a, b[a]

Test Solvent	Solubility[b] Parameter, δ	Polymer V a	VI a	VII a	V b	VI b	VII b
Toluene	8.90	I	I	I	I	I	I
Ethyl acetate	9.07	I	I	I	I	I	I
Chloroform	9.21	PS	PS	PS	PS	PS	PS
NMP	11.17	PS	S	S	S	S	PS
DMF	12.15	PS	PS	PS	S	S	S
DMSO	13.04	PS	PS	PS	S	S	S
Methanol	14.49	I	I	I	I	I	I
Water	23.43	I	I	I	I	I	I

[a] I = insoluble; PS = partially soluble; S = soluble; [b] Solvent solubility parameter in $(\mathrm{Cal/cm^3})^{1/2}$ [10].

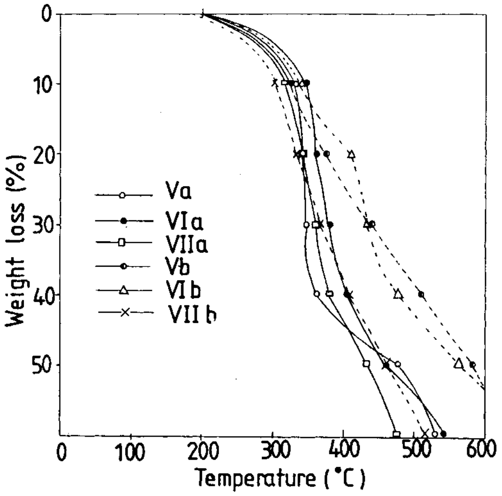


Figure 3. TGA curves of polymers V-VII a, b.

The crystallinity of the PAMU was studied by X-ray diffractions measurements (Figure 2). The PAMU from ortho-series (V-VII b) showed a semicrystalline behavior and the peaks occuring in the curve of the monomer IIb are still present in the polymers diffraction curves. The PAMU from para-series (V a-VI a) seems to be either semicrystalline or amorphous, respectively. The solubility behavior of PAMU V-VII a, b at room temperature is given in Table 2.

As can be seen, the polymers V-VII b had good solubility in aprotic dipolar solvents such as NMP, DMF, DMSO, greater than that of the polymers V-VII a, probably due to the reduced close packing of the former polymers. From the solubility tests, the solubility parameter values seems to be reasonable estimated in the 11.17-13.04 $(Cal/cm^3)^{1/2}$ range.

The thermal behavior of the PAMU (V-VII a, b) was also studied by thermogravimetric analysis (TGA) in air (Figure 3). The weight loss occurred in two well-defined steps as similar reported [4, 5]. As can be seen from Table 1, the PAMU from V-VIIa series had higher T_{10} values than the V-VII b ones, probably due to the well known difference which exists between the polymers containing para-substituted phenylene rings (that means extended conjugation and strong intermolecular interactions), and those containing metha- (in our case ortho-substituted phenylene rings) which possessed lower levels of conjugation and intermolecular interactions [4]. Considering the influence of the diisocyanate structure on the thermal stability, the following order of T_{10} values can be stated for both series of PAMU: VI > V > VII. The polymers VII a, b containing long aliphatic groups in the backbone naturally had much less thermal stability.

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