SOME POLYURETHANES BASED ON UNSATURATED POLYESTERS

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ABSTRACT: The present paper discusses the synthesis of linear unsaturated polyesters by the polycondensation reaction of maleic anhydride with different glycols (ethylene glycol, diethylene glycol, triethylene glycol, 1,4-butane diol, 1,6-hexane diol and neopenthyl glycol) with acidities less than 5 mg KOH/g of sample, and the possibility to decrease the cross-linking process during reaction. The polyester-diols with relatively high molecular weight (~2000) were characterized by IR, ^{1}H-NMR, end - groups analysis, as well as by the double bond content determination. These unsaturated polyesters may be used alone or in combination with other diols or diamines in synthesis of segmented polyurethanes. The presence of the unsaturated polyester as soft segment in the polyurethane chain might result in potential applications in several domains such as synthesis of different block copolymers, thermosetting resins, plasticizers, biodegradable and controlled release systems, etc. The polyurethanes were characterized by infrared (IR) and ^{1}H-NMR spectroscopy, stress-strain measurements and other technique.

KEYWORDS: *unsaturated polyester segmented polyurethane, polycondensation*

INTRODUCTION

Unsaturated polyesters as macroglycols or polyols are used for synthesis of polyester and copolyester - based urethane rubbers [1, 2]. The presence of the unsaturated polyester as soft segment in the polyurethane chain might result in potential applications in several domains such as synthesis of different block copolymers, thermosetting resins, plasticizers, biodegradable and controlled release systems, etc. The unsaturated polyesters may be used alone or in combination with other diols (diamines) in synthesis of segmented polyurethanes The polymers based on linear OH-terminated polyesters, 4,4'-diphenylmethane-diisocyanate (MDI), and a glycol as chain extender (1:1 ratio of NCO/OH groups), reveal excellent elastomer properties and can be processed as thermoplastics [3].

The unsaturated polyesters are usually obtained by polycondensation of combined mixtures of unsaturated diacides (anhydrides) and diols. The inclusion of the unsaturated bond into polymer backbone (often through acidic component) makes possible a subsequent curing of the resin to polymeric materials with improved physico-chemical properties [4]. Such polyesters had been already prepared by direct polyesterification method [5, 6].

The synthesis of unsaturated polyesters derived from maleic anhydride is relatively difficult, as side and branching reactions may occur. The polycondensation process, carried out under normal conditions (trough the melt method), is accompanied by an isomerization reaction of maleate to fumarate form [7]. Increasing of the fumarate form percentage in the final product is due to the glycol segments favouring *cis-trans* transformation [8]. As a consequence of methylene group numbers increasing [9], this isomerization became weaker in the ethylene glycol -1,6-hexane diol series, (between 66% to 25%).

In the maleic anhydride based unsaturated polyesters synthesis process, branching reactions may occur, because of the glycol segments or final OH end groups addition to the double bond [10]. Some authors consider that in this reaction about 15% of polymeric chain unsaturation might be consumed [11, 12]. These results suggest that the intramolecular spatial interactions appear also as a consequence of the neighbouring position of the ester groups, and not only as a result of the steric hindrance of the hydroxyl group, or due to the length of the glycol.

EXPERIMENTAL

Materials:
- Maleic anhydride (MA, local mark), recrystallized from chloroform, mp 52 ^{o};
- Adipic acid (AA, Aldrich), Fw =146.14; mp=152-154 ^{o}; bp = 265 ^{o}/100 mm, used without further purification;
- Propylene glycol (PG, Aldrich), Fw76.10, mp –60 ^{o}, bp 187 ^{o}, n_D^{20} 1.4320, d 1.036, used without further purification;
- Butane diol (BD, Fluka) mp=16 ^{o}; bp 230 ^{o}; n_D^{20} = 1.4450; d=1.017, Merck, used without further purification;

- Hexanediol (HD, Merk); mp 41-43 ^{o}; bp 250 ^{o}; Merck, used without further purification;
- Neopentyl glycol (NPG, Aldrich), Fw 104.15, mp 123-127 ^{o}, used without further purification;
- Ethylene glycol (EG, local mark) refluxed with sodium for 1 hour, then distilled at atmospheric pressure, the 190-192 ^{o} fraction being collected;
- Diethylene glycol (DEG, Aldrich) Fw 106.12, mp –10 ^{o}, bp 245 ^{o}, n_D^{20} 1.4460, d 1.118, used without further purification;
- Triehtylene glycol (TEG, Aldrich), Fw 150.17, mp –7 ^{o}, bp 285 ^{o}, n_D^{20} 1.4550, d 1.125, used without further purification;
- Toluene diisocyanate (TDI, Aldrich), Fw 174.16, mp 20-22 ^{o}, bp 120 ^{o}/10 mm, n_D^{20} 1.5680, d 1.214, fresh distilled;
- Diphenyl methane diisocyanate (MDI Aldrich), fresh distilled, Fw 250.26, mp 42-44 ^{o};
- Dibenzyl diisocyanate (DBDI, local mark), fresh distilled, Fw 264, mp 62-65 ^{o};
- Dimethylformamide, purified and dried by vacuum distillation on 4,4'-BDBI, b_p=153 ^{o}; n_D=1.4295.
- Different solvents.

Synthesis of polyesters

The reaction may be represented by:
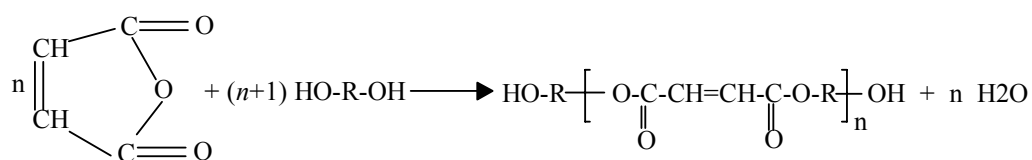
Where:

R= $-CH_2-CH_2-$; $-CH_2-CH_2-CH_2-CH_2-$; $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$;
    $-CH_2-CH_2-O-CH_2-CH_2-$; $-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-$;
    $-CH_2-C(CH_3)_2-CH_2-$; $-CH_2-CH_2-CH_2-$.

The reaction was carried out in a 250 cm^{3} four-necked flask, equipped with mechanical stirring, contact thermometer and bubbling tube for dry nitrogen.
Polycondensation was accomplished in benzene, water being removed from the reaction by steaming. The solvent was separated and reutilised.
Typical, MA or MA and AA (in different amount) and different mole glycol (EG, BD, DEG, HD, NPG), with molar ratio presented in Table 1, 150 ml benzene was used. The mixture was pre-condensed for 2 hours under reflux, after that the water resulted from reaction was collected. The reaction was stopped when the differences between two acidity measurements became insignificants. The solvent was removed by distillation, and then the mixture was vacuum dried at 60 ^{o}C. The

final composition of the polyesters was determined from NMR and IR spectral analysis. The acidities and OH number of the solid polyesters were determined by titration method.

Table 1. Composition and characteristics of polyesters

Composition of polyester	C_{OH}, mgKOH/g	I_{AC}, mgKOH/g	Mn g/mol	$DB*10^4$, mg Br/g
P1 (MA: AA: PG 1:1:2,5)	56	2,5	2000	4.50
P2 (MA: AA: BD 1:1:2,5)	56	2	2000	4.25
P3 (MA: AA: HD 1:1:2,5)	56	2,8	2000	3.50
P4 (MA: AA: NPG 1:1:2,5)	54	1,6	2074	3.83
P5 (MA: AA: DEG 1:1:2,5)	58	3	1931	3.78
P6 (MA: EG 1:2)	112	2,0	1000	9.63
P7 (MA: PG 1:2)	160	2,7	700	8.50
P8 (MA: BD 1:2)	56	2,4	2000	7.25
P9 (MA: NPG 1:2)	112	3,0	1000	6.81
P10 (MA: DEG 1:2)	224	2,5	500	6.75
P11 (MA:TEG 1:2)	56	2,0	2000	4.88
P12 (MA: HD 1:1,1)	56	2,8	2000	6.20
P13 (MA: EG: BD 1:1:1)	56	2,0	2000	8.44
P14 (MA: EG: PG 1:0,5:0,6)	54	2,3	2074	9.00
P15 (MA: EG: DEG 1: 0,5:0,6)	55	3,2	2037	7.88
P16 (MA: EG: TEG 1: 0,5:0,6)	56	3,5	2000	7.13
P17 (MA: EG: HD 1: 0,5:0,6)	57	2,7	1965	7.50
P18 (MA: EG: NPG 1: 0,5:0,6)	55,8	2,4	2007	7.94
P19 (MA: BD: PG 1: 0,6:0,5)	56	2,7	2000	7.87
P20 (MA: BD: DEG 1:0,5:0,6)	56	3,2	2000	7.12
P21 (MA: BD: TEG 1:0,5:0,6)	54	2,5	2074	6.00
P22 (MA: BD: HD 1:0,6:0,5)	58	2,0	1930	6.78
P23 (MA: BD: NPG 1:0,6:0,5)	56	2,4	2000	6.88
P24 (MA: DEG: TEG 1:0,4:0,7)	56	2,6	2000	5.88
P25 (MA: DEG: HD 1:0,5:0,6)	56	2,4	2000	6.38
P26 (MA: DEG: NPG 1:0,5:0,6)	56	2,3	2000	6.75
P27 (MA: PG: DEG 1:0,6:0,5)	53,5	1,8	2090	7.44
P28 (MA: PG: TEG 1:0,6:0,5)	56	2,3	2000	6.44
P29 (MA: PG: HD 1:0,6:0,5)	54	2,9	2074	7.23
P30 (MA: PG: NPG 1:0,5:0,6)	56	2,3	2000	7.56
P31 (MA: TEG: HD 1:0,6:0,5)	52	1,4	2154	5.56
P32 (MA: TEG: NPG 1:0,5:0,6)	56	1,5	2000	5.88
P33 (MA: HD: NPG 1:0,5:0,6)	56	2,4	2000	6.50

Purification of polyesters

After the reaction was stopped, part of polymer was solved in acetone and filtered through a G4 filter. The filtered solution was heated up to boiling, and then petroleum ether was added (60 – 80 ^{o}C) until the reaction mixture became opalescent. The mixture was than cooled at room temperature and the polymeric

part was separated. This material was finally dried under vacuum (0.1 Torr) at 60 ^{o}C for 3 hours. In this mode were purified all polyesters.

Synthesis of polyurethanes

Typical, the polyol was dried under vacuum for 2 h at 120 ^{o}C. In next phase the polyol is cooled at 90 ^{o}C when the solvent, and diisocyanate is added at molar ratio polyol: diisocyanate showed in Table 2, for 2 h to form a prepolymer. Then the diol was added into the prepolymer with rapid stirring at 90 ^{o}C for 10 min followed by more stirring at room temperature for 3 h to complete the reaction. The final concentration of PU in solvent was between 25-40% by weight.
The mixture was carefully poured into casting mould and the latter placed in an air oven. The curing cycle comprised three stages, each of 24 h at 60 ^{o}C, 90 ^{o}C and 120 ^{o}C, respectively. All polyurethanes were prepared in same mode.

Analytical techniques

The polyester's molecular weight was determined by quantitative measurements of the OH and COOH end-groups content in according with methods presented in previously paper [12].
Double bond content was determined by the sulphite method [13]: two samples of the compound and other two blanks were considered in temperature and pressure resistant Erlenmeyer flasks, 25 ml of (2M) sodium sulphite saturated solution were introduced, then 25.0 ml of 1N sulphuric acid were pipetted and finally 15 ml of isopropyl alcohol were added. Two flasks were retained as blanks; in the other two, measured quantities of sample (which should not contain more than 15 milleq. of unsaturated compound) were introduced. The reactions were carried out at 98 ^{o}C for 90 minutes. Then, the flasks were cooled at -10 ^{o}C for 10 minutes. Subsequently, 5-6 drops of indicator (Brome Thimol Blue) were added and the samples were titrated with 0.5 N NaOH solution until the indicator changed colour.
The IR spectra were run on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellets.
H NMR spectroscopy- samples were analyzed in $CDCl_3$ on a C 80 HL type High Resolution NMR Instrument, using tetramethylsilane as internal standard.


RESULTS AND DISCUSSION

^{1}H NMR and IR spectra confirmed the structures of unsaturated polyesters.
Figure 1 present the ^{1}H NMR spectra only for P6, P9 and P10 samples, considered the most representative.

Table 2. Composition and the characteristics of the polyurethanes

| Composition of polyurethane	Solvent utilised	Concentration in dried polymer, %	Stress at break, (Compact film) daN/cm^2
P1: EG: MDI 1:4:5	DMF	28	7,00
P2: EG: MDI 1:4:6	DMF	30	6,20
P3: PG: MDI 1:4:5	DMF	32	5,70
P4: BG:TDI 1:4:5	DMF:AcEt 7:1	40	3,75
P5: NPG:MDI 1:4:5	DMF:Tol 6:1	28	8,82
P6: DEG:MDI 1:4:5	DMF	33	5,14
P7:DEG:TDI 1:4:5	AcEt:Tol 5:1	40	3,12
P8:HD:MDI 1:4:5	DMF	33	2,20
P9:TEG:TDI 1:4:5	AcEt:Ac 4:1	40	2,75
P10:DEG:TDI 1:3:4	AcEt	40	2,78
P11:TEG:TDI 1:5:6	AcEt:Ac 5:1	40	4,52
P12:HD:TDI 1:5:6	AcEt	40	3,24
P13:BG:MDI 1:4:5	DMF:MEK 4:1	35	3,85
P14:EG:MDI 1:4:5	DMF:Xy 5:1	33	5,45
P15:TEG:TDI 1:6:7	DMF	30	4,55
P16:EG:MDI 1:5:6	DMF	33	3,22
P17:HD:TDI 1:7:8	DMF	25	6,45
P18: NPG:TDI 1:7:8	DMF	25	5,64
P19: BG:MDI 1:6:7	DMF	26	4,66
P20: DEG:MDI 1:6:7	DMF:Tol 7:1	28	3,41
P21:TEG:TDI 1:7:8	DMF	30	4,25
P22:BG:MDI 1:4:5	DMF:MEK 7:1	28	3,41
P23:NPG:DBDI 1:3:2	DMF	34	3,42
P24:TEG:TDI 1:7:8	AcEt:Ac 8:1	40	3,52
P25:HD:TDI 1:7:8	DMF:Tol 7:1	30	5,41
P26:NPG:TDI 1:5:6	DMF:Tol 7:1	30	3,20
P27: DEG:MDI 1:7:8	DMF	30	4,28
P28:TEG:TDI 1:7:8	AcEt	40	2,80
P29:PG:TDI 1:7:8	AcEt	40	3,94
P30:NPG:MDI 1:3:4	AcEt	40	2,75
P31:NPG:MDI 1:4:5	DMF	30	3,39
P32:NPG:MDI 1:6:7	DMF	30	5,45
P33:TEG: TDI 1:8:9	AcEt	40	6,28

Table 3 presents the interpretation of the ^{1}H NMR spectra for only P6, P9 and respectively P10 unsaturated polyesters, the *cis-trans* ratio, and their proportion of ramification structures.

We observed some differences for ratio of *cis-trans* structures, and to the degree of branching of the unsaturated polyesters, which believe appears for different ionisation of the glycols in reaction medium and steric and electronic effects between glycols and MA. The solubility of the reaction components is it another cause.
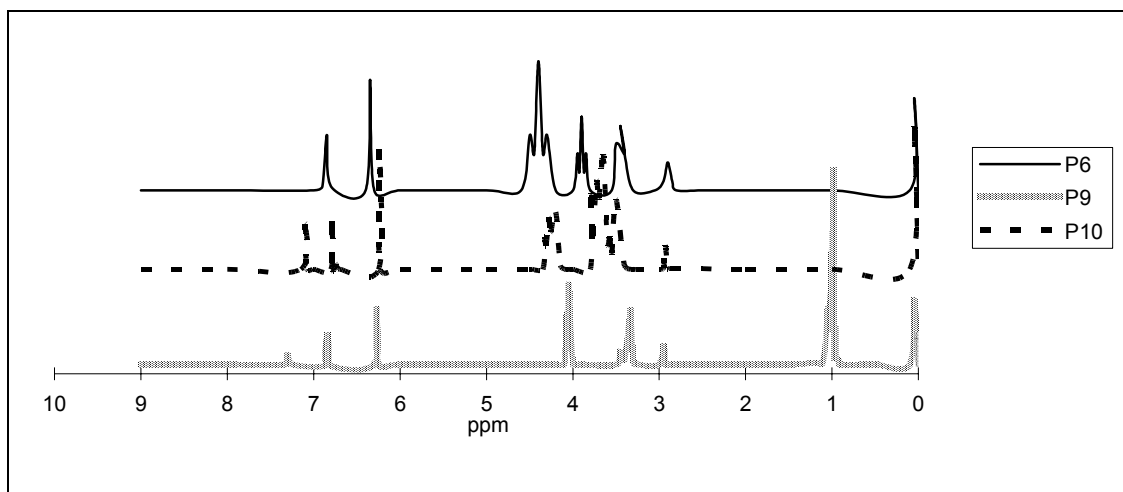
Figure 1. ^{1}H NMR spectra for P6, P9 and P10 (see Table 1)

Table 3 Interpretation of the H NMR spectra for P6, P9 and P10 unsaturated polyesters

Polyester	Peak, ppm	Attribution	Observation	*Cis-trans* ratio, moles	Proportion of ramification, %
P6	2,90 3,90 4,40 6,30 6,85	-OH -CH$_2$- -CH$_2$- -CH=CH- -CH=CH-	terminal inner *cis* *trans*	1 : 1	10-12
P9	1 2,95 3,35 4,1 6,25 6,8	-CH$_3$ -OH -CH$_2$ -CH$_2$ -CH=CH- -CH=CH-	terminal inner cis trans	2:1	5-6
P10	2,90 3,5-3,8 4,1-4,4 6,25 6,85	-OH -CH$_2$-CH$_2$- -CH$_2$-CH$_2$- -CH=CH- -CH=CH-	terminal inner *cis* *trans*	1,5 : 1	1-2

The difficulty results from the fact that *cis-trans* isomerization occurs simultaneously with the polycondensation reaction, through a cationic intermediate:
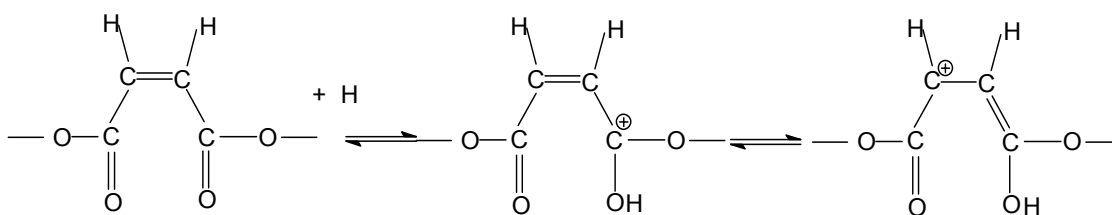
This intermediate may facilitate the addition of a hydroxyl group to the olefinic double bond.
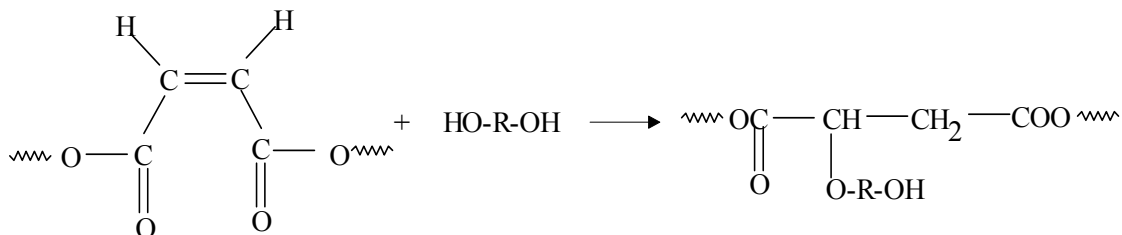
Where:

R= -CH$_2$-CH$_2$- ; -CH$_2$-CH$_2$-CH$_2$-CH$_2$- ; -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$- ;
    -CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-; -CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-;
    -CH$_2$-C(CH$_3$)$_2$-CH$_2$-; -CH$_2$-CH$_2$-CH$_2$-.

Figures 2 and 3 present the ^{1}H NMR and IR spectrum only for polyurethane based on P6/DEG/MDI with molar ratio 1:4:5 considered the most representative, confirmed the formation of the unsaturated segmented polyurethanes.
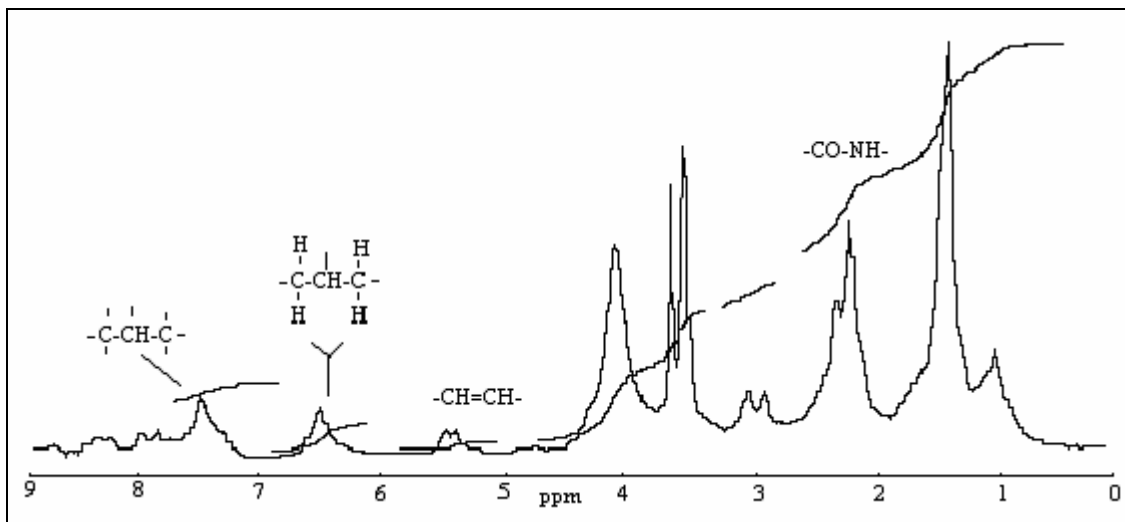

Figure 2. ^{1}H NMR spectrum for polyurethane based on P6/DEG/MDI
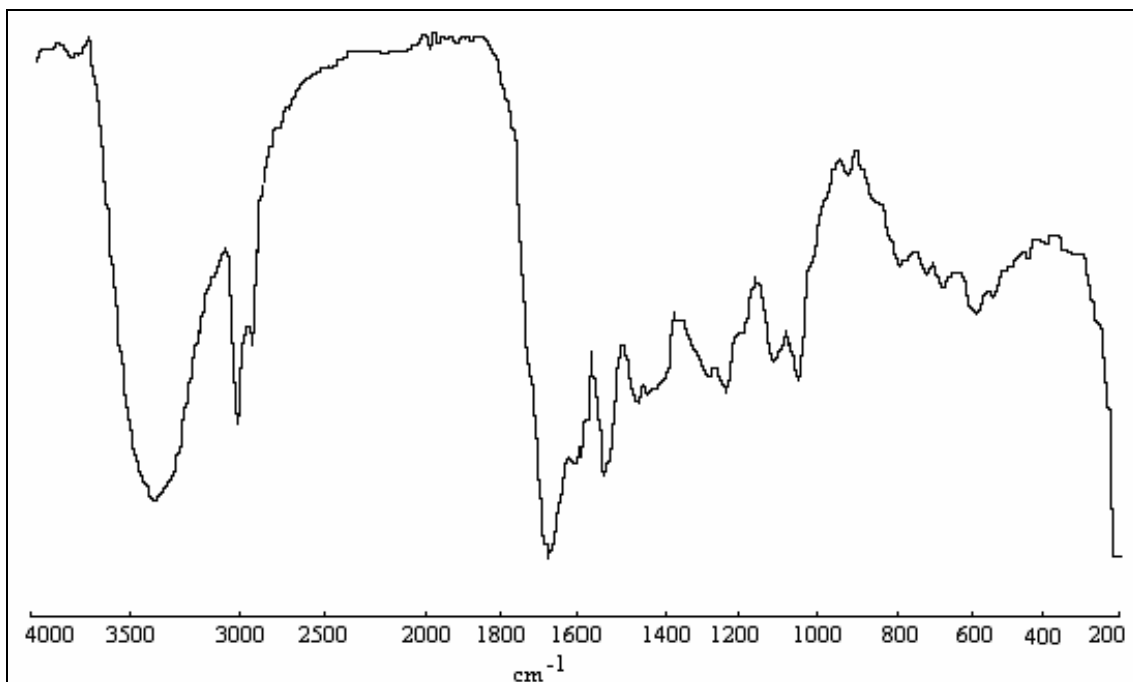with molar ratio 1:4:5

Figure 3. IR spectrum for polyurethane based on P6/DEG/MDI
with molar ratio 1:4:5

The signal corresponding to NCO group (2270 cm^{-1}) is absent in this spectrum.

CONCLUSION

Although under normal synthesis conditions (the melt method), the obtainment of an based maleic anhydride unsaturated polyester and different glycols is difficult, in solution the process is simpler, linear unsaturated polyesters with a low degree of branching and molecular weights up to 2000 thus resulting.

These unsaturated polyesters can be used for the preparation of the segmented polyurethanes.

The segmented polyurethanes prepared from the unsaturated polyesters and different diisocyanate constitutes a family of performance materials. These materials have interesting physical properties. The application range increases permanent, covering materials for biomedicine, vibration dampening materials, abrasion and thermal resistant coatings.

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