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FT-IR STUDY OF POLY(ETHER)URETHANES

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Defence R&D Canada

Technical Memorandum

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FT-IR STUDY OF POLY(ETHER)URETHANES

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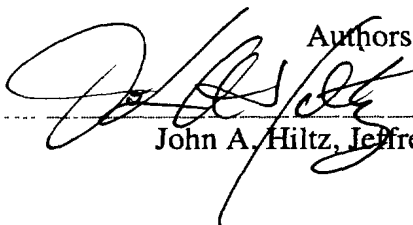
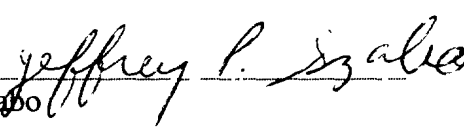
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Abstract

The infrared (IR) spectra of sixteen 4,4-methylenebis(phenyl isocyanate) (MDI) based and four 1,6-diisocyanatohexane (HDI) based poly(ether)urethane (AB)_n block copolymers are presented. Differences in the IR spectra of these polymers are related to differences in the diols and polyether glycols and the ratios of reactants used to synthesize them. IR spectroscopy can distinguish between the MDI and HDI poly(ether)urethanes and identify the diols and polyether glycols used to prepare the polymers. The intensity of the amide I bands (non-hydrogen bonded and hydrogen) are found to depend on the hard segment weight fraction of the polymers and are indicative of the degree of hydrogen bonding in the polymers. The relative intensity of the C-O stretches in the hard and soft segments of the polymers were found to increase with hard segment weight fraction.

Résumé

On présente les spectres infrarouges (IR) de copolymères séquences de poly(éther)uréthanes (AB)_n, soit seize à base de 4,4'-méthylènebis(phénylisocyanate) (MDI) et quatre à base de 1,6-diisocyanatohexane (HDI). On a établi des corrélations entre les différences observées dans les spectres IR de ces polymères et les différences dans les diols et les polyétherglycols et les proportions de réactifs utilisés pour les synthétiser. La spectroscopie IR permet de distinguer les poly(éther)uréthanes à base de MDI de ceux à base de HDI et d'identifier les diols et les polyétherglycols utilisés pour les synthétiser. On a constaté que l'intensité des bandes amide I (avec et sans liaison hydrogène) dépend de la fraction massique de segments rigides des polymères et donne une indication du degré de liaison hydrogène dans ces polymères. On a aussi constaté que l'intensité relative des vibrations C-O dans les segments rigides et souples des polymères augmentait avec la fraction massique de segments rigides.

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Executive summary

Introduction

The development and application of semi-empirical modeling techniques to predict the properties of polymeric materials is an active area of research. Confidence in the predictions of these models requires that they be verified with results from actual compounds. For group contribution and additive techniques, the synthesis and characterization of a series of compounds with well defined chemistry is necessary to evaluate the contribution of structural units to the observed properties. In this paper, the infrared (IR) spectra of sixteen 4,4'-methylenebis(phenyl isocyanate) (MDI) based and four 1,6-diisocyanatohexane (HDI) based poly(ether)urethane (AB)_n block copolymers are presented. These polyurethanes were synthesized as part of a study of the applicability of Group Contribution Theory and Group Interaction Modeling to the prediction of dynamic mechanical properties of poly(ether)urethanes. Differences in the IR spectra of these polymers are related to differences in the diols and polyether glycols and the ratios of reactants used to synthesize them. Differences in the IR spectra of the poly(ether)urethanes can also give insight into differences in the microstructure of the compounds which have an affect on the dynamic mechanical properties of the polymers.

Principal Results

The results indicate that IR spectroscopy can distinguish between the MDI and HDI poly(ether)urethanes and identify the diols and polyether glycols used to prepare the polymers. The intensity of the amide I bands (non-hydrogen bonded and hydrogen bonded) were found to depend on the hard segment weight fraction of the polymers and are indicative of the degree of hydrogen bonding in the polymers. The relative intensity of the C-O stretches in the hard and soft segments of the polymers were found to increase with hard segment weight fraction. The nature of the diol, the molecular weight of the polyether glycol, the degree of hydrogen bonding and weight percent hard segment have a significant effect on the microstructure and therefore the properties of poly(ether)urethane block copolymers.

Significance of Results

IR spectroscopy is one of several characterizations techniques that will be used to probe the structure of this series of poly(ether)urethanes. As the properties of these materials are very dependent on their structure, this information will be useful in the study of the application of modeling techniques to the prediction of poly(ether)urethanes properties.

Hiltz, J. A. and Szabo, J. P. 2001.FT-IR Study of Poly(ether)urethanes. DREA TM 2001-073. Defence Research Establishment Atlantic.

Sommaire

Introduction

L'élaboration de techniques de modélisation semi-empiriques de matériaux polymériques et leur application à la prévision de leurs propriétés est un domaine de recherche en pleine activité. Il est indispensable de vérifier les prévisions de ces modèles au moyen de résultats obtenus avec de véritables composés, pour pouvoir les utiliser en toute confiance. Pour les techniques de contribution des groupes et les techniques additives, la synthèse et la caractérisation d'une série de composés présentant une structure chimique bien définie sont nécessaires pour évaluer dans quelle mesure les unités structurales contribuent aux propriétés observées. Dans cet article, on présente les spectres infrarouges (IR) de copolymères séquences de poly(éther)uréthanes (AB)_n, soit seize à base de 4,4'-méthylènebis(phénylisocyanate) (MDI) et quatre à base de 1,6-diisocyanatohexane (HDI). Ces polyuréthanes ont été synthétisés dans le cadre d'une étude sur l'applicabilité de la théorie de contribution des groupes et de la modélisation de l'interaction des groupes à la prévision des propriétés mécaniques dynamiques des poly(éther)uréthanes. On a établi des corrélations entre les différences observées dans les spectres IR de ces polymères et les différences dans les diols et les polyétherglycols et les proportions de réactifs utilisés pour les synthétiser. Les différences observées dans les spectres IR de ces poly(éther)uréthanes peuvent aussi renseigner sur les différences de microstructure de ces composés, différences qui influent sur les propriétés mécaniques dynamiques des polymères.

Principaux résultats

Les résultats obtenus ont montré que la spectroscopie IR permet de distinguer les poly(éther)uréthanes à base de MDI de ceux à base de HDI et d'identifier les diols et les polyétherglycols entrant dans leur préparation. On a constaté que l'intensité des bandes amide I (avec et sans liaison hydrogène) dépend de la fraction massique de segments rigides de ces polymères et donne une indication du degré de liaison hydrogène dans ces polymères. On a aussi constaté que l'intensité relative des vibrations C-O dans les segments rigides et souples de ces polymères augmentait avec la fraction massique de segments rigides. La nature du diol, la masse moléculaire du polyétherglycol, le degré de liaison hydrogène et la fraction massique de segments rigides ont un effet important sur la microstructure et, donc, sur les propriétés des copolymères séquences de poly(éther)uréthanes.

Importance des résultats

La spectroscopie IR est une technique de caractérisation parmi plusieurs qui sera utilisée pour étudier la structure de cette série de poly(éther)uréthanes. Comme les propriétés de ces matériaux dépendent étroitement de leur structure, les renseignements obtenus seront utiles pour l'étude de l'application de techniques de modélisation permettant de prévoir les propriétés des poly(éther)uréthanes.

Hiltz, J. A. and Szabo, J. P. 2001. FT-IR Study of Poly(ether)urethanes. DREA TM 2001-073. Defence Research Establishment Atlantic.

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Introduction

The use of modelling techniques to predict the properties of polymeric materials prior to synthesis is an area of great interest. Bicerno [1] notes that “the ability to predict the key physical and chemical properties of polymers prior to synthesis is of great value in the design of polymers”. Semi-empirical modeling techniques include topological techniques [1], Group Interactive Modeling [2], and additive contribution techniques [3]. More recently with the development of parallel and scalable codes it is possible to use quantum mechanical codes to model larger systems [4].

Confidence in the predictions of these modeling techniques requires that they be verified using data from actual compounds. For group contribution or additive techniques, the synthesis and characterization of a series of compounds is required to evaluate the contributions of structural groups to the observed properties. One group of compounds that our Laboratory is interested in modeling and characterizing are the poly(ether)urethane thermoplastic elastomers.

Thermoplastic poly(ether)urethane elastomers are $(AB)_n$ segmented block copolymers synthesized from a diisocyanate, a diol chain extender, and a polyether glycol. The isocyanate rich or hard segments (A) of the elastomer have a higher glass transition temperature than the polyether glycol rich or soft segments (B) of the elastomer. The hard segments act as virtual cross-links for the soft segments of the block copolymer and are responsible for their elastomeric properties [5].

The isocyanate and polyether rich portions of poly(ether)urethanes are incompatible and therefore tend to phase separate. The degree of phase separation (or alternatively phase mixing) is dependent on a number of factors including the chemical structures of the reactants, the molecular weights of the components and their ratios [6-9], the

synthesis method [10], and the processing history of the elastomer [11]. By varying these factors it is possible to prepare a series of elastomers with a wide range of thermal and mechanical properties [12].

Infrared (IR) spectroscopy has been applied to the characterization of poly(ether)urethanes (13-16). IR characterization can provide information about the chemical nature of poly(ether)urethanes, that is, the reactants used to prepare the elastomer and their relative concentrations, and the level of hydrogen bonding in the elastomer. This is important because the level of phase separation in polyurethanes, which affects their mechanical and thermal properties, is related to the level of hydrogen bonding.

In this paper the IR spectra of a series of polyurethanes are presented and discussed with respect to how changes in reactants and reactant concentrations are reflected in the IR spectra. These polyurethanes were synthesized as part of a study of the applicability of Group Contribution Theory and Group Interaction Modeling to the prediction of the dynamic mechanical properties of poly(ether)urethanes.

Experimental

The 20 polyurethane samples are listed in Table 1. The structures of the reactants used to prepare the samples are shown in Figure 1. The polyurethanes were prepared using one of two diisocyanates, 4,4'-methylenebis(phenyl isocyanate) (MDI) or 1,6-diisocyanatohexane (HDI); one of three diols, 1,4-butanediol (BDO), diethylene glycol (DEG), or 2,2-dimethyl-1,3-propanediol (DMPD); and one of two polyols, poly(tetramethyleneether glycol) or poly(ethylene glycol). The poly(tetramethylene ether glycol)s had molecular weights of 650 (T650), 1000 (T1000), and 1400 (T1400). The poly(ethylene glycol)s had molecular weights of 600 (P600) and 1000 (P1000). Two of the samples (#1 and #13) were synthesized using only a diisocyanate and a diol and one sample (#16) from a diisocyanate and a poly(tetramethylene ether glycol). These samples are not block copolymers. Therefore samples #1 and #13 contain only hard segments and sample #16 only soft segments.

The polyurethanes were synthesized by BodyCote Ortech, Mississauga, Ontario [17]. All syntheses were carried out in dimethylformamide.

Infrared spectra were acquired on a Nicolet model 510P Fourier transform infrared (FT-IR) spectrometer in the transmission mode. The samples were spotted on NaCl plates and the solvent (dimethylformamide) evaporated prior to analysis. Typically 32 scans were acquired and the resolution was 4 cm^{-1} . Following background subtraction, the spectra were normalized to 1.0 absorbance unit (10% transmittance) for the most intense band.

Table 1. Molar ratios of reactants used to prepare polyurethane samples #1 to #18.

	BDO	T650	T1000	T1400	DEG	P600	P1000	DMPD	MDI	HDI
Mol Weight	90.122	639	978	1376	106.12	590	982	104.15	250.25	168.19
1	1								1	
1R	1								1	
2	1							1		2
3			1					0.5	1.5	
4			1					5	6	
5				1				1	2	
6				1				5	6	
7					1			1		2
8						1		0.5	1.5	
9							1	1	2	
9R							1	1	2	
10							1	5	6	
11							1	5		6
13					1				1	
13R					1				1	
14		1						5	6	
16			1						1	
16R			1						1	
17			1					3	4	
18			1					3		4

Results and Discussion

The results for MDI and HDI based polyurethanes are discussed separately.

MDI Based Polyurethanes

The IR spectra of MDI based poly(ether)urethanes are characterized by amide I bands (C=O stretch) at $\sim 1730\text{ cm}^{-1}$ and $\sim 1705\text{ cm}^{-1}$, an amide II band (mixed mode vibration resulting from out-of-phase combination of OCN and NH vibrations) at $\sim 1530\text{ cm}^{-1}$, C-O stretches at $\sim 1220\text{ cm}^{-1}$, $\sim 1110\text{ cm}^{-1}$, and $\sim 1070\text{ cm}^{-1}$, a C=C stretch (MDI aromatic ring) at 1598 cm^{-1} , and a N-H stretch at $\sim 3315\text{ cm}^{-1}$. The absorption frequency of the amide I C=O stretch is sensitive to the level of hydrogen bonding in the polymer [15,18]. Hydrogen bonding shifts the C=O stretch to lower frequencies. The amide I bands at $\sim 1730\text{ cm}^{-1}$ and $\sim 1705\text{ cm}^{-1}$ are due to non-hydrogen bonded and hydrogen bonded amide groups respectively. The C-O stretches are attributed to the carbonyl carbon and adjacent oxygen, the polyether oxygen and adjacent carbon, and the oxygen adjacent to the carbonyl carbon and the adjacent carbon [13,14]. The absorption frequency of the N-H stretch is also sensitive to hydrogen bonding. A non hydrogen bonded N-H stretch has a frequency of $\sim 3440\text{ cm}^{-1}$ [18]. Hydrogen bonding reduces the frequency to between 3340 cm^{-1} and 3260 cm^{-1} .

The IR spectra of the MDI based polyurethanes are shown in Figures 2 through 17.

Model MDI Based Polyurethanes Containing Only 'Hard' or 'Soft' Segments

Samples #1, #1R, #13, and #13R were synthesized using only MDI and a diol. The IR spectra of these samples are shown in Figures 2, 3, 12, and 13 respectively. Because these polymers do not contain a polyether glycol, their IR spectra are representative of the hard segment portion of a poly(ether)urethane. In contrast to these samples,

samples #16 and #16R were synthesized from a polyether glycol and MDI. Their IR spectra are shown in Figures 15 and 16. Because they contain no diol, their IR spectra are representative of the soft segment portion of a poly(ether)urethane.

Assignment of the IR bands of samples #1, #1R, #13, #13R, #16 and #16R are shown in Figure 18. The infrared spectra of samples #1 and #1R have an amide I band at 1701 cm^{-1} but no amide I band at $\sim 1730\text{ cm}^{-1}$. This is consistent with the hard segment nature of these polyurethanes and indicates that the amide groups in these polymers are hydrogen bonded. Similarly, samples #13 and #13R exhibited a single amide I band at 1708 cm^{-1} , indicating that the amide groups are hydrogen bonded in these samples. Samples #16 and #16R have two amide I bands at 1732 cm^{-1} and 1713 cm^{-1} . The relative intensity of these bands indicates that most of the amide groups are not hydrogen bonded. However the band at 1713 cm^{-1} does indicate that some hydrogen bonding is taking place.

The frequency of the N-H stretch for these samples ($\sim 3320\text{ cm}^{-1}$ to 3300 cm^{-1}) is also consistent with hydrogen bonding in these compounds.

Samples #1 and #13 have a band at $\sim 1075\text{ cm}^{-1}$, while sample #16 has an intense band at 1110 cm^{-1} with a shoulder at $\sim 1075\text{ cm}^{-1}$. These bands are attributable to C-O stretches. The band at 1075 cm^{-1} is due to C-O stretch in urethane portion of the polymer and the band at 1110 cm^{-1} is due to a C-O stretch in the polyether glycol portion of the polymer.

Samples #1, #1R, #13, #13R, #16 and #16R have bands at $\sim 1597\text{ cm}^{-1}$ (C=C aromatic in-plane vibration), at $\sim 1529\text{ cm}^{-1}$ (amide II band), at $\sim 1413\text{ cm}^{-1}$ (CH_2 scissoring), at $\sim 1311\text{ cm}^{-1}$ (C-N vibration aromatic secondary amine), at $\sim 1223\text{ cm}^{-1}$ (C-O stretch), at $\sim 816\text{ cm}^{-1}$ (benzene ring with two adjacent hydrogens), and $\sim 770\text{ cm}^{-1}$ (CH_2 rocking). Samples #16 and #16 R also had bands at $\sim 2941\text{ cm}^{-1}$, $\sim 2856\text{ cm}^{-1}$, and

$\sim 2795\text{ cm}^{-1}$ (C-H stretches), and $\sim 1367\text{ cm}^{-1}$ (CH_2 deformation) that arise from the polyether glycol portion of the polymer.

T1000/DMPD/MDI Poly(ether)urethanes

The IR spectra of the three T1000/DMPD/MDI poly(ether)urethanes, samples #3, #4, and #17, are shown in Figures 4, 5 and 17 respectively. Assignment of the IR bands for these poly(ether)urethanes are shown in Figure 19.

Differences in these three poly(ether)urethanes arise as the result of different ratios of the reactants used to prepare them and these differences are reflected in their IR spectra. For instance the ratio of the intensity of hydrogen bonded to non-hydrogen bonded amide I bands increase as weight percent MDI, and therefore percent hard segment, in the compounds increase. The increase in percent hard segment results in increased phase separation. This in turn results in an increase in hydrogen bonding between urethane rich hard segments.

The hard segment weight fractions for samples #3, #4, and #17 are listed in Table 2 along with the ratio of the intensities of the hydrogen bonded to non hydrogen bonded amide I bands and the ratio of the intensities of the hard and soft segment C-O stretches at $\sim 1065\text{ cm}^{-1}$ and $\sim 1110\text{ cm}^{-1}$. The hard segment weight fraction of the polyurethanes was calculated according to method shown in reference 19.

The ratio of the intensities of the bands at $\sim 1710\text{ cm}^{-1}$ and $\sim 1730\text{ cm}^{-1}$ and at $\sim 1065\text{ cm}^{-1}$ and $\sim 1110\text{ cm}^{-1}$ increase with hard segment weight fraction. The bands at $\sim 1710\text{ cm}^{-1}$ and $\sim 1065\text{ cm}^{-1}$ arise from the hydrogen bonded amide I C=O stretch and C-O stretch for the hard segments of these poly(ether)urethanes. Conversely, the bands arising from the soft segment (polyether glycol rich) portion of the polymer decrease as the hard segment weight fraction increases. For instance, the intensity of the bands

at $\sim 2940\text{ cm}^{-1}$, $\sim 2860\text{ cm}^{-1}$, and $\sim 2995\text{ cm}^{-1}$ (C-H stretches) decrease with increasing hard segment weight fraction.

Table 2. Hard segment weight fraction and ratios of the intensities of IR bands at $\sim 1710\text{ cm}^{-1}$ and $\sim 1730\text{ cm}^{-1}$ and $\sim 1065\text{ cm}^{-1}$ and 1110 cm^{-1} for poly(ether)urethane samples #3, #4, and #17.

SAMPLE #	MOLAR RATIOS T1000/DMPD/MDI	HARD SEGMENT WEIGHT FRACTION (%)	ABSORBANCE RATIO	ABSORBANCE RATIO
			AMIDE I BANDS $1710\text{ cm}^{-1}/1730\text{ cm}^{-1}$	C-O STRETCH $1065\text{ cm}^{-1}/1110\text{ cm}^{-1}$
3	1.0/0.5/1.5	32.4	0.63	0.61
4	1.0/5.0/6.0	68.0	1.12	1.67
17	1.0/3.0/4.0	58.3	0.96	1.23

The three polymers have bands at $\sim 1597\text{ cm}^{-1}$ (C=C aromatic in-plane vibration), $\sim 1535\text{ cm}^{-1}$ (amide II band), $\sim 1413\text{ cm}^{-1}$ (CH_2 scissoring), $\sim 1311\text{ cm}^{-1}$ (C-N vibration aromatic secondary amine), $\sim 1220\text{ cm}^{-1}$ (C-O stretch), and $\sim 816\text{ cm}^{-1}$ (benzene ring with two adjacent hydrogens) can be attributed to the urethane rich portion of the polymers.

T1400/DMPD/MDI Poly(ether)urethanes

The IR spectra of the two T1400/DMPD/MDI poly(ether)urethanes, samples #5 and #6, are shown in Figures 6 and 7. Assignment of their IR bands is shown in Figure 19. The hard segment weight fraction, ratio of intensities of the amide I bands, and ratio of the intensity of the C-O stretches at 1065 cm^{-1} and 1110 cm^{-1} are given in Table 3. As was observed for the poly(ether)urethanes containing polyether glycol T1000, the ratio of intensities of the hydrogen bonded and non hydrogen bonded

amide I bands and the C-O stretches at $\sim 1065\text{ cm}^{-1}$ and $\sim 1110\text{ cm}^{-1}$ increase with hard segment weight fraction.

Table 3. Hard segment weight fraction and ratios of the intensities of IR bands at 1710 cm^{-1} and 1730 cm^{-1} and 1065 cm^{-1} and 1110 cm^{-1} for poly(ether)urethane samples #5 and #6.

SAMPLE #	MOLAR RATIOS T1400/DMPD/MDI	HARD SEGMENT WEIGHT FRACTION (%)	ABSORBANCE RATIO AMIDE I BANDS $1710\text{ cm}^{-1}/1730\text{ cm}^{-1}$	ABSORBANCE RATIO C-O STRETCH $1065\text{ cm}^{-1}/1110\text{ cm}^{-1}$
5	1.0/1.0/2.0	31.8	0.57	0.58
6	1.0/5.0/6.0	60.0	0.96	1.30

Effect of Polyether Glycol Molecular Weight on the IR Spectra of Polyether glycol/DMPD/MDI (1/5/6) Poly(ether)urethanes

The molar ratios of the reactants used to prepare samples #14, #4, and #6 were the same. These polymers differ only in the molecular weight of the polyether glycol used in their preparation; T650 has a molecular weight of 650 (sample #14), T1000 a molecular weight of 1000 (sample #4), and T1400 a molecular weight of 1400 (sample #6). A change in molecular weight of the polyether glycol affects the hard segment weight fraction of the polymer. The hard segment weight fraction of samples #14, #4, and #6 along with the ratios of the intensities of amide I bands and the C-O stretches at $\sim 1065\text{ cm}^{-1}$ and $\sim 1110\text{ cm}^{-1}$ are shown in Table 4.

The ratio of the intensities of the hydrogen bonded to non hydrogen bonded amide I bands decrease as the hard segment weight fraction of the elastomers decrease. Similarly the ratio of the intensities of the C-O stretches at 1065 cm^{-1} and $\sim 1110\text{ cm}^{-1}$ decrease as the hard segment weight fraction of the elastomers decrease.

The intensity of the C-H stretching bands (2940 cm^{-1} , 2860 cm^{-1} , 2795 cm^{-1} , and 1370 cm^{-1}) increase with an increase in the molecular weight of the polyether glycol and reflect the increase in the number of $-\text{CH}_2-$ units in the polymer.

Table 4. Hard segment weight fraction and ratios of the intensities of IR bands at 1710 cm^{-1} and 1730 cm^{-1} and 1065 cm^{-1} and 1110 cm^{-1} for poly(ether)urethane samples #14, #4, and #6.

SAMPLE #	MOLECULAR WEIGHT POLYETHER GLYCOL	HARD SEGMENT WEIGHT FRACTION (%)	ABSORBANCE RATIO AMIDE I BANDS $1710\text{ CM}^{-1}/1730\text{ CM}^{-1}$	ABSORBANCE RATIO C-O STRETCH $1065\text{ CM}^{-1}/1110\text{ CM}^{-1}$
14	650	76.9	1.22	2.28
4	1000	68.0	1.12	1.67
6	1450	60.0	0.96	1.30

Correlation of Amide I Band Intensities with Hard Segment Weight Fraction of PTMO/DMPD/MDI Poly(ether)urethanes

Seymour et. al. [15] observed that the ratio of the intensities of the hydrogen bonded and non hydrogen bonded amide I could be used to determine the level of hydrogen bonding in a series of poly(ether) urethanes. Changes in the ratio were related to changes in the urethane rich hard segment concentration and the degree of phase separation in the polymers. A plot of the ratio of the hydrogen bonded and non-hydrogen bonded amide I band intensities for the PTMO/DMPD/MDI poly(ether)urethanes (samples #3, #4, #5, #6, #14, and #17) against hard segment weight fraction of the polymers is shown in Figure 20. An excellent correlation is observed. The intensity of the hydrogen bonded amide I band (relative to the non-hydrogen bonded amide I) increases with an increase in the hard segment weight fraction.

P1000/DMPD/MDI Poly(ether)urethanes

The IR spectra of the P1000/DMPD/MDI poly(ether)urethane samples #9, #9R, and #10 are shown in Figures 9 through 11 respectively. The IR band assignments for these samples are shown in Figure 21. The bands arising from the hard segment portion of these poly(ether)urethanes are the same as those observed for the poly(tetramethylene ether) glycol (PTMO) based DMPD/MDI poly(ether)urethanes. For instance, the bands at $\sim 1728\text{ cm}^{-1}$ (non hydrogen bonded amide I band), $\sim 1599\text{ cm}^{-1}$ (C=C aromatic in-plane vibration), $\sim 1536\text{ cm}^{-1}$ (amide II band), $\sim 1413\text{ cm}^{-1}$ (CH_2 scissoring), $\sim 1311\text{ cm}^{-1}$ (C-N vibration aromatic secondary amine), $\sim 1223\text{ cm}^{-1}$ (C-O stretch), $\sim 1072\text{ cm}^{-1}$ (C-O stretch), and $\sim 816\text{ cm}^{-1}$ (benzene ring with adjacent hydrogens) arise from the hard segment of the polymers. Samples #9 and #9R do not have hydrogen bonded amide I bands. Sample #10 has non-hydrogen bonded (1728 cm^{-1}) and hydrogen bonded (1709 cm^{-1}) amide I bands.

These compounds have IR bands arising from the polyethylene glycol rich portion of the polymer at $\sim 1105\text{ cm}^{-1}$ (C-O stretch), 1349 cm^{-1} (C-H deformation), and $\sim 2870\text{ cm}^{-1}$ (C-H stretch).

Table 5. Hard segment weight fraction and ratios of the intensities of IR bands at 1072 cm^{-1} and 1105 cm^{-1} for poly(ether)urethane samples #9, #9R, and #10.

SAMPLE #	MOLAR RATIOS P1000/DMPD/MDI	HARD SEGMENT WEIGHT FRACTION (%)	ABSORBANCE RATIO C-O STRETCH $1072\text{ CM}^{-1}/1105\text{ CM}^{-1}$
9	1.0/1.0/2.0	39.8	0.85
9R	1.0/1.0/2.0	39.8	0.85
10	1.0/5.0/6.0	68.0	1.59

The ratio of the intensity of the IR bands at 1072 cm^{-1} and 1105 cm^{-1} for poly(ether)urethane samples #9, #9R, and #10 are listed in Table 5. As was observed for the PTMO/DMPD/MDI poly(ether)urethanes, the ratio increases as the hard segment weight fraction increases. Two amide I bands were observed for sample #10. The ratio of their intensities was 0.88.

P600/DMPD/MDI Poly(ether)urethane

The IR spectrum of sample #8 is shown in Figure 8 and the assignment of the IR bands is shown in Figure 21. The IR spectrum is similar to those for samples #9 and #9R. This sample has bands at $\sim 1728\text{ cm}^{-1}$ (non hydrogen bonded amide I band), $\sim 1599\text{ cm}^{-1}$ (C=C aromatic in-plane vibration), $\sim 1536\text{ cm}^{-1}$ (amide II band), $\sim 1413\text{ cm}^{-1}$ (CH_2 scissoring), $\sim 1311\text{ cm}^{-1}$ (C-N vibration aromatic secondary amine), $\sim 1223\text{ cm}^{-1}$ (C-O stretch), $\sim 1072\text{ cm}^{-1}$ (C-O stretch), and $\sim 816\text{ cm}^{-1}$ (benzene ring with two adjacent hydrogens) that arise from the hard segment of the polymer. There is no distinct hydrogen bonded amide I band.

This compound has IR bands arising from the polyethylene glycol rich portion of the polymer at $\sim 1105\text{ cm}^{-1}$ (C-O stretch), 1349 cm^{-1} (C-H deformation), and $\sim 2870\text{ cm}^{-1}$ (C-H stretch).

HDI based polyurethanes

The IR spectra of the samples HDI based polyurethanes are shown in Figures 22 through 25 respectively.

HDI Based Polyurethanes with no Poly(ether)glycol

The IR spectra of samples #2 and #7 are shown in Figures 22 and 23. These polyurethanes were prepared using two diols, sample #2 BDO and DMPD and sample #7 DEG and DMPD, and no polyether glycol. The IR band assignments for these

samples are shown in Figure 26. These IR spectra are characterized by amide I bands ($\sim 1697\text{ cm}^{-1}$ for sample and $\sim 1684\text{ cm}^{-1}$ for sample #7), amide II bands ($\sim 1537\text{ cm}^{-1}$), and C-O stretches ($\sim 1253\text{ cm}^{-1}$ for sample #2 and 1261 cm^{-1} for sample #7).

The frequency of the amide I band ($\sim 1697\text{ cm}^{-1}$ and $\sim 1684\text{ cm}^{-1}$ for samples #2 and #7 respectively) and N-H stretch ($\sim 3317\text{ cm}^{-1}$ and 3324 cm^{-1} for samples #2 and #7 respectively) is consistent with a significant level of hydrogen bonding [18,20] in these polyurethanes.

P1000/DMPD/HDI and T1000/DMPD/HDI Polyetherurethanes

The IR spectra of samples #11 (P1000/DMPD/HDI (1/5/6)) and sample #18 (T1000/DMPD/HDI (1/3/4)) are shown in Figures 24 and 25 respectively. In contrast to sample #2 and #7, the IR spectra have bands that are characteristic of the polyether glycol used in their preparation. The intense bands at $\sim 2933\text{ cm}^{-1}$ and $\sim 2868\text{ cm}^{-1}$ in sample #11 and at $\sim 2936\text{ cm}^{-1}$, $\sim 2858\text{ cm}^{-1}$, and $\sim 2795\text{ cm}^{-1}$ in sample #18 arise from C-H stretches in the soft segment (polyether glycol rich) portion of the polyurethane. Sample #18 also has a band at 1368 cm^{-1} due to the CH_2 deformation in the soft segment of the polymer.

The frequencies of the amide I band (1704 cm^{-1}) and N-H stretch (3336 cm^{-1}) of sample #11 are indicative of hydrogen bonding in this sample. Sample #18 has two amide I bands (1720 cm^{-1} and 1704 cm^{-1}). This indicates that some of the amide groups are not hydrogen bonded.

Conclusions

Infrared (IR) spectroscopy has been used to differentiate between sixteen 4,4'-methylenebis(phenyl isocyanate) (MDI) based and four 1,6-diisocyanatohexane (HDI) based poly(ether)urethanes. The IR spectra provide information on the reactants, that is, the diisocyanate, diol and polyether glycol, and the ratio of the reactants used to prepare the poly(ether)urethanes.

The IR spectra of PTMO/DMPG/MDI based polyurethanes are characterized by amide I bands at $\sim 1730\text{ cm}^{-1}$ (non hydrogen bonded) and $\sim 1705\text{ cm}^{-1}$ (hydrogen bonded), an amide II band at $\sim 1535\text{ cm}^{-1}$, an aromatic C=C in-plane vibration at $\sim 1597\text{ cm}^{-1}$, C-O stretches at $\sim 1225\text{ cm}^{-1}$ and $\sim 1065\text{ cm}^{-1}$, C-N vibration of a secondary aromatic amine at $\sim 1311\text{ cm}^{-1}$, and bands at $\sim 1410\text{ cm}^{-1}$, $\sim 816\text{ cm}^{-1}$, and $\sim 770\text{ cm}^{-1}$ arising from CH₂ scissoring, a benzene ring with two adjacent hydrogens and CH₂ rocking respectively. The bands at $\sim 1110\text{ cm}^{-1}$ (C-O stretch), $\sim 2941\text{ cm}^{-1}$, $\sim 2856\text{ cm}^{-1}$, and $\sim 2795\text{ cm}^{-1}$ (C-H stretches), and $\sim 1367\text{ cm}^{-1}$ (CH₂ deformation) arise from the polyether glycol (PTMO) portion of the polymer.

The ratio of the hydrogen and non hydrogen bonded amide I band intensities increases with weight fraction of the hard segment for the MDI based polyurethanes.

The position of the CH₂ deformation and C-H stretch arising from the polyether glycol portion of the PEG/DMPD/MDI polyurethanes can be used to distinguish them from the PTMO/DMPD/MDI polyurethanes. The CH₂ deformation for the PEG/DMPD/MDI polyurethanes is at $\sim 1348\text{ cm}^{-1}$ compared to 1367 cm^{-1} for the PTMO/DMPD/MDI polyurethanes. In addition, the PEG/DMPD/MDI polyurethanes have only one C-H stretch at $\sim 2840\text{ cm}^{-1}$ compared to three C-H stretches for the PTMO/DMPD/MDI polyurethanes at 2940 cm^{-1} , 2860 cm^{-1} , and 2795 cm^{-1} .

For both PTMO/DMPD/MDI and PEG/DMPD/MDI poly(ether)urethanes the ratio of the intensity of the bands at $\sim 1065\text{ cm}^{-1}$ and 1110 cm^{-1} increases with an increase in the hard segment weight fraction of the polymer.

HDI and MDI based poly(ether)urethanes are easily differentiated on the basis of their IR spectra. The peaks arising from the aromatic rings in the MDI portion of the polymer (C=C aromatic vibration at $\sim 1597\text{ cm}^{-1}$, C-N vibration of a secondary aromatic amine at $\sim 1311\text{ cm}^{-1}$, and the band at 816 cm^{-1} due to a benzene ring with two adjacent hydrogens) are not present in the spectra of HDI based poly(ether)urethanes. The position of C-O stretch (carbonyl carbon and adjacent oxygen) shifts from $\sim 1223\text{ cm}^{-1}$ for the MDI based poly(ether)urethanes greater than 1250 cm^{-1} for the HDI based poly(urethanes).

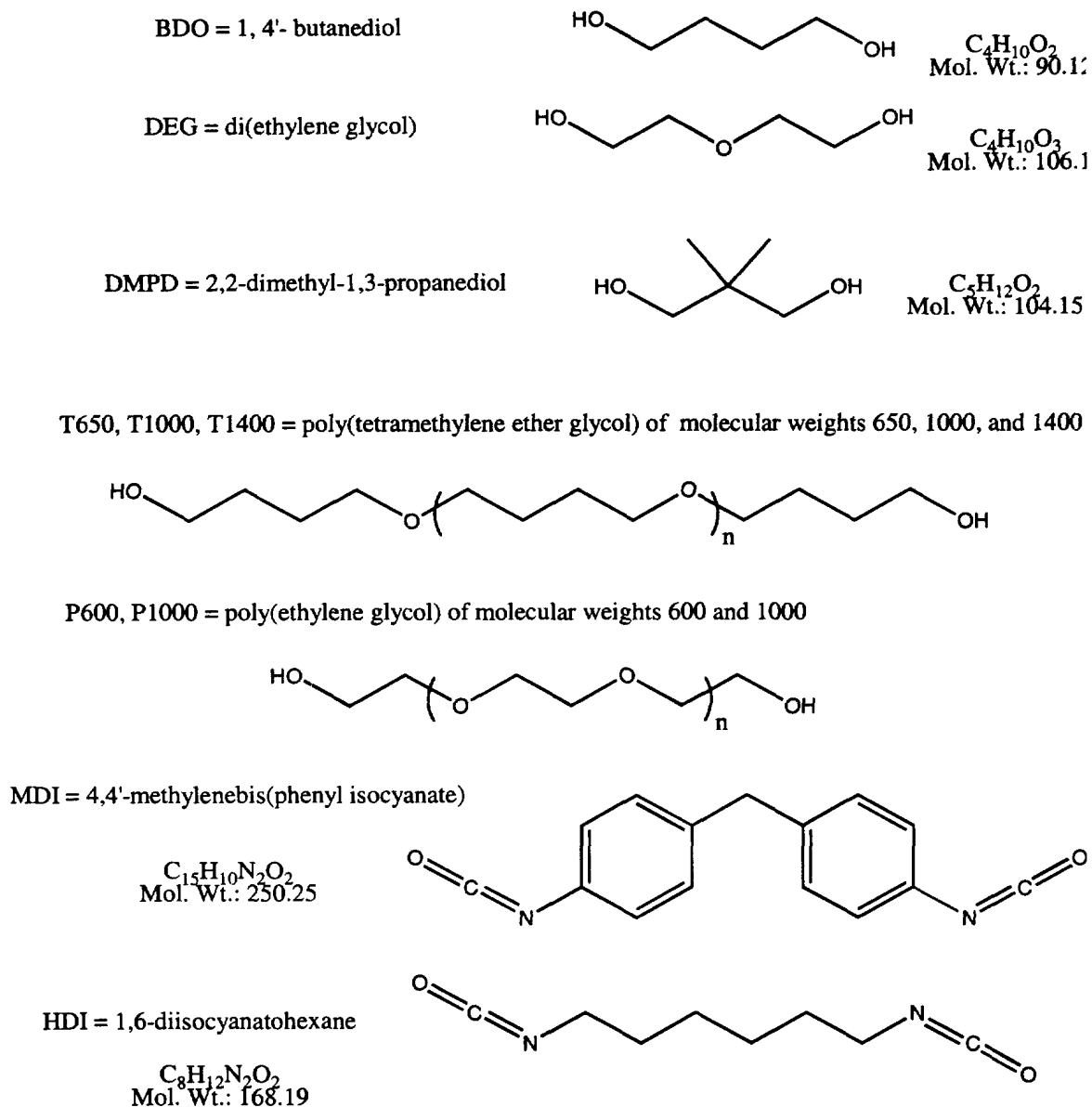


Figure 1. Structure of the reactants used to prepare polyurethane samples #1 to #18.

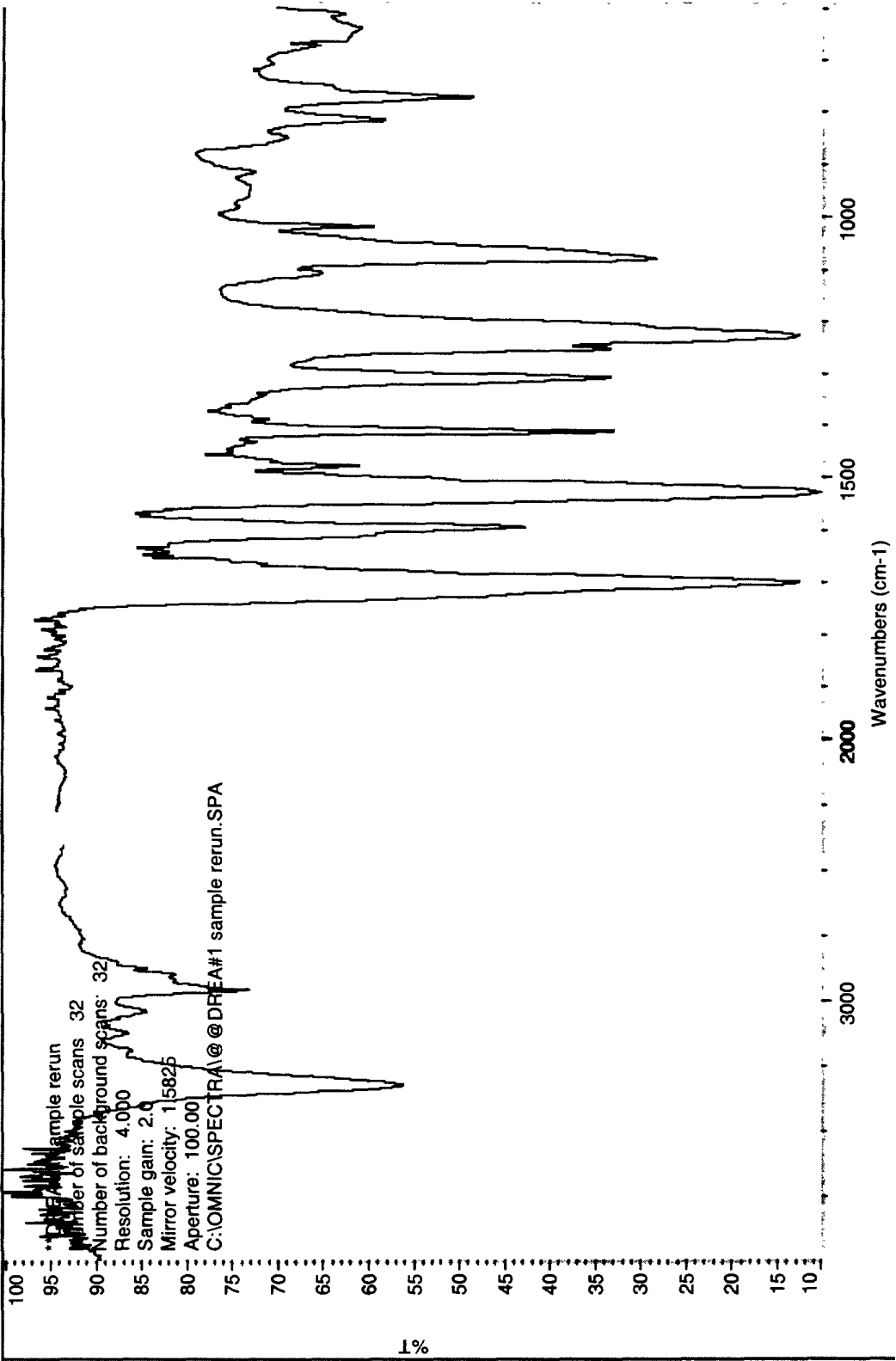


Figure 2 Infrared spectrum of polyurethane sample #1 - BDO/MDI (1/1).

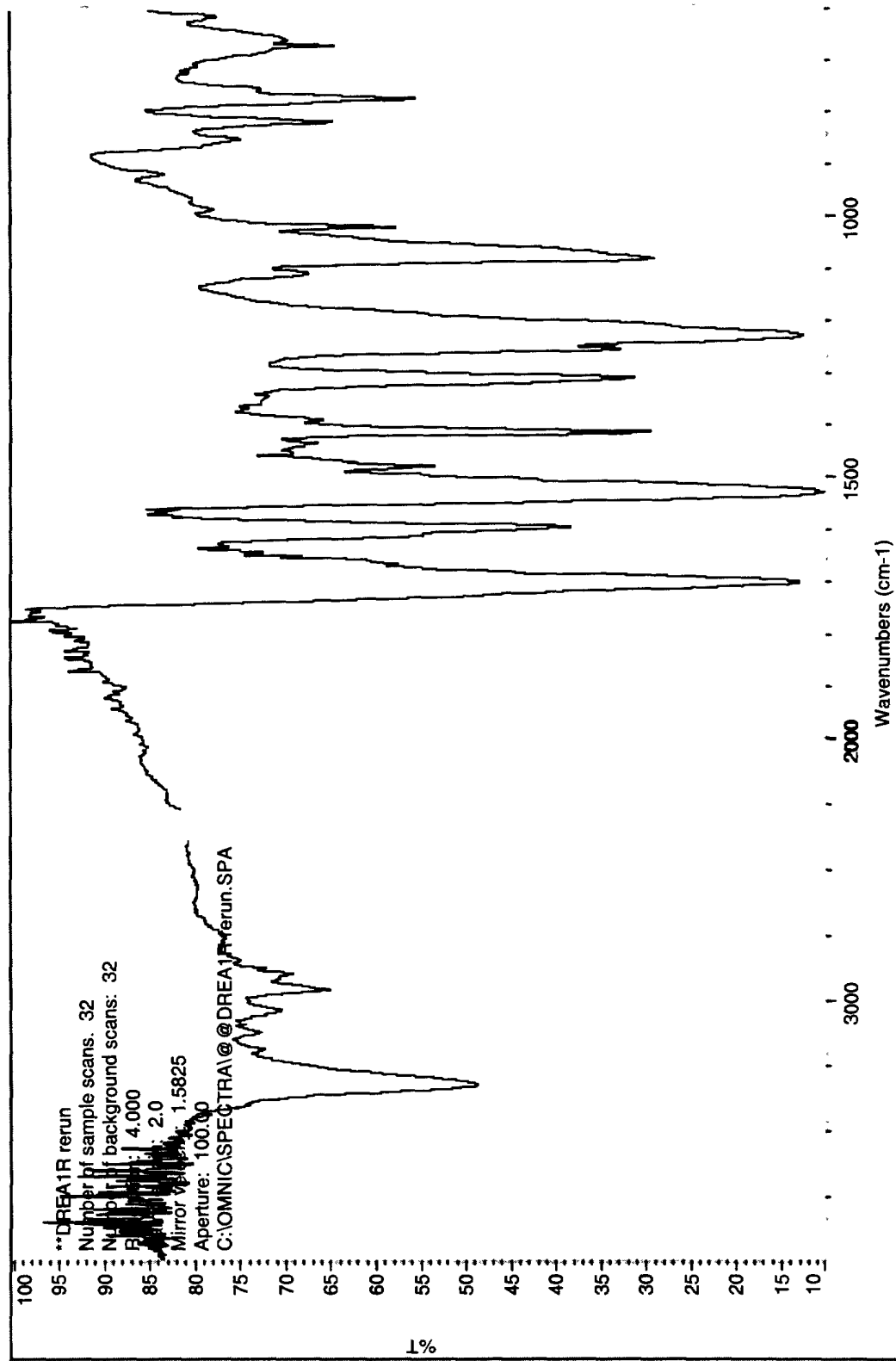


Figure 3 Infrared spectrum of polyurethane sample #1R - BDO/MDI (1/1).

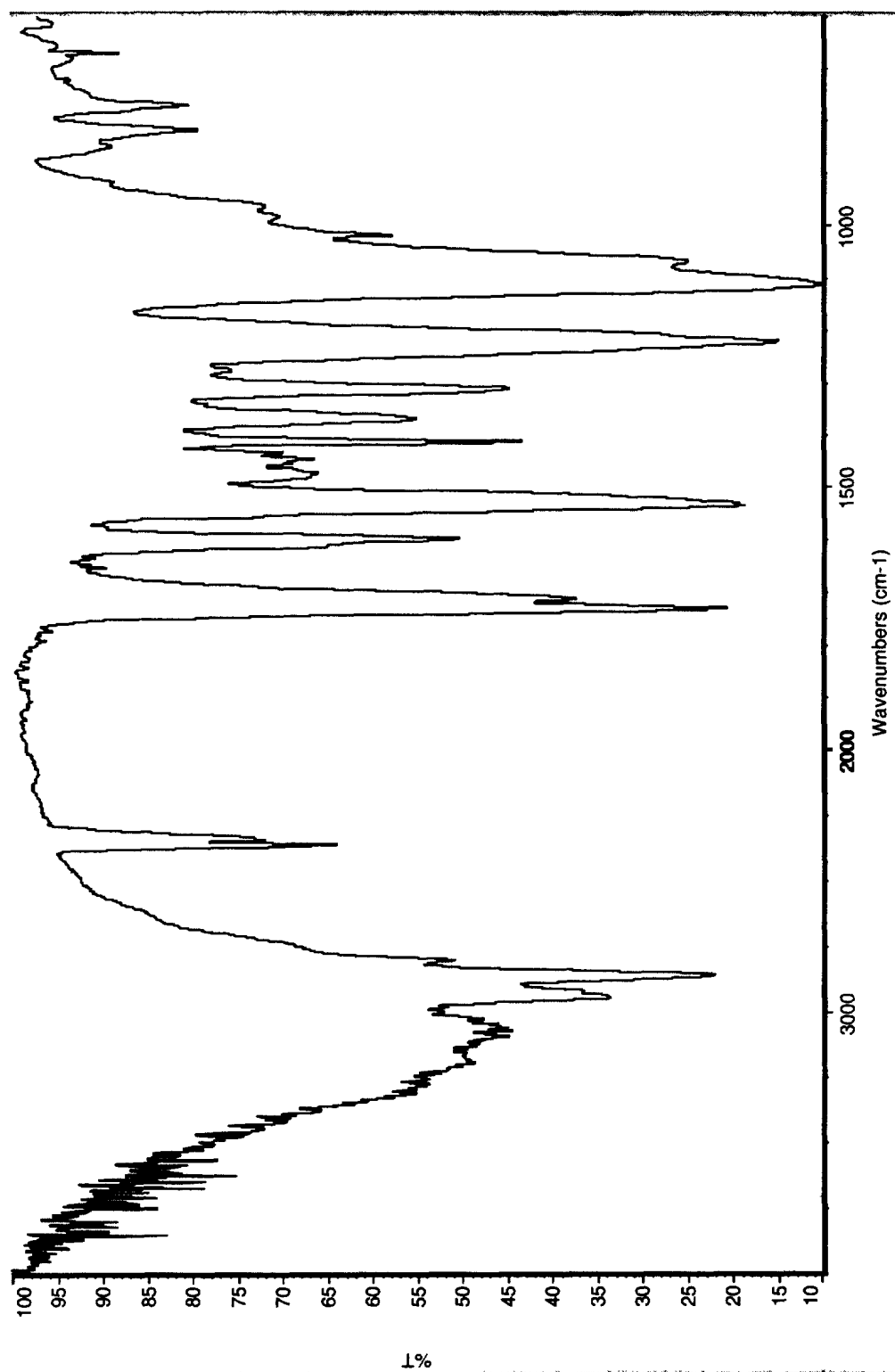


Figure 4. Infrared spectrum of polyurethane sample #3 - T1000/DMPD/MDI (1.0/0.5/1.5).

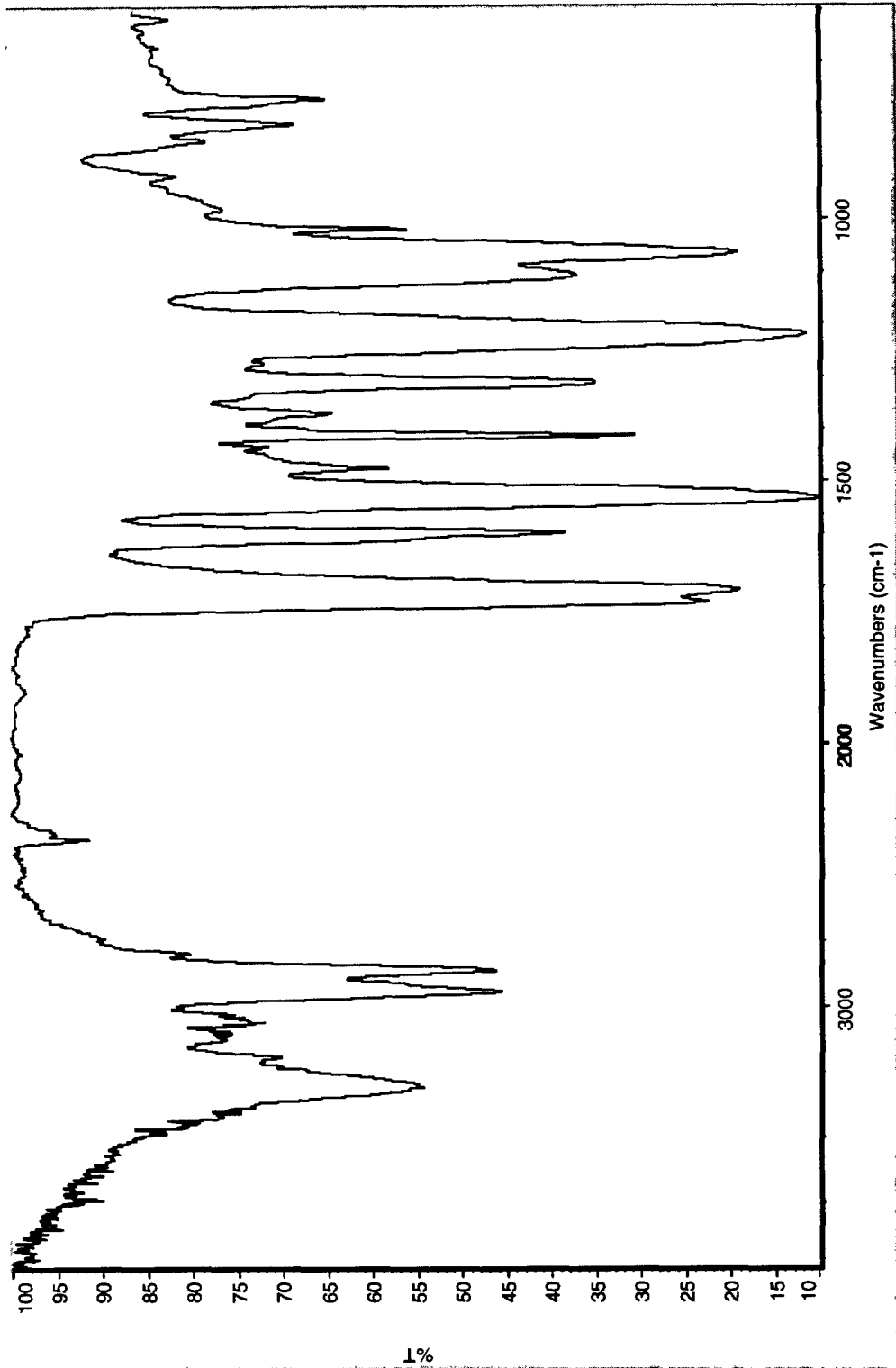


Figure 5 - Infrared spectrum of polyurethane sample #4 - T1000/DMPG/MDI (1.0/5.0/6.0).

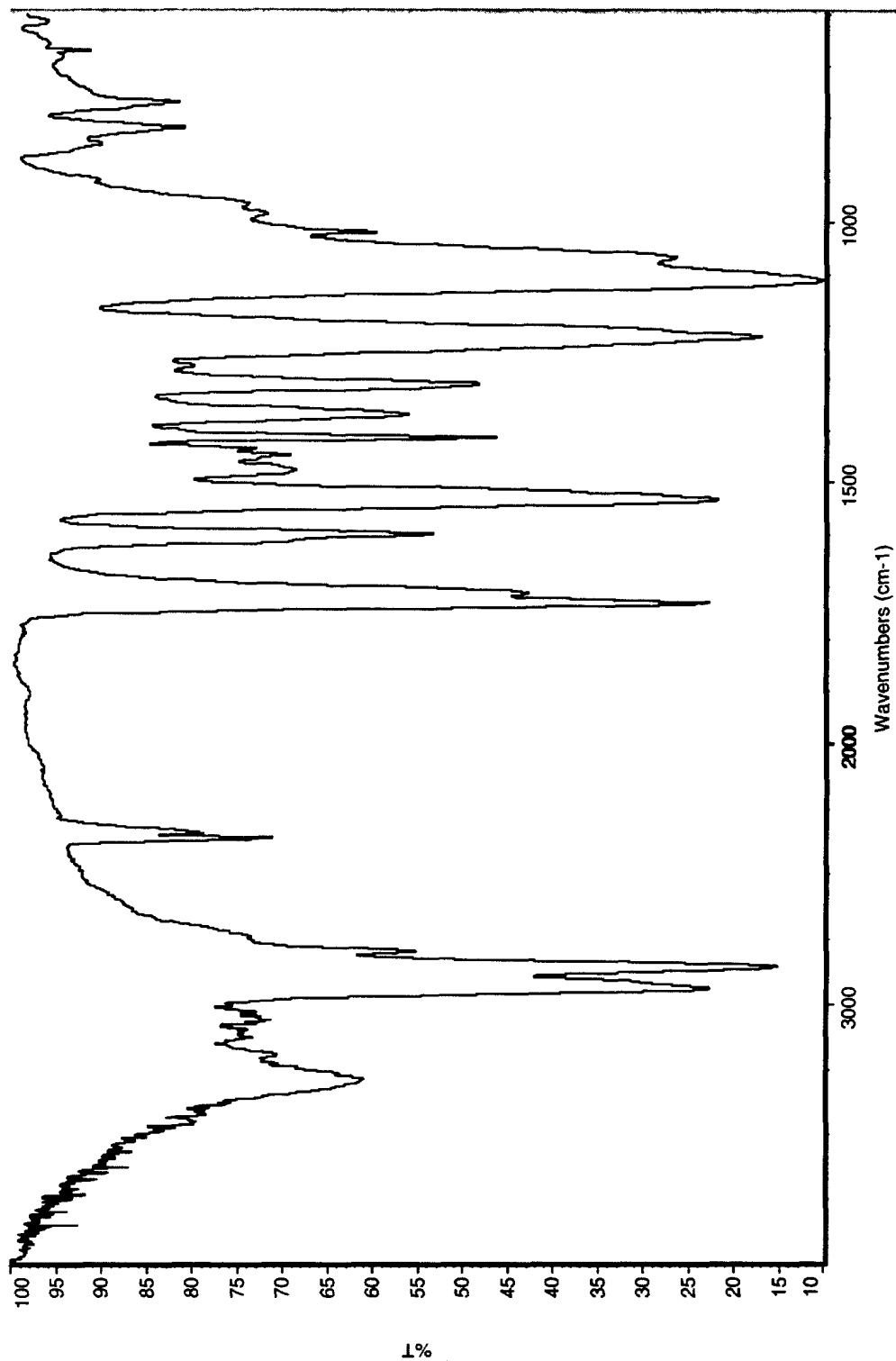


Figure 6 - Infrared spectrum of polyurethane sample #5 - T1400/DMPGMDI (1.0/1.0/2.0).

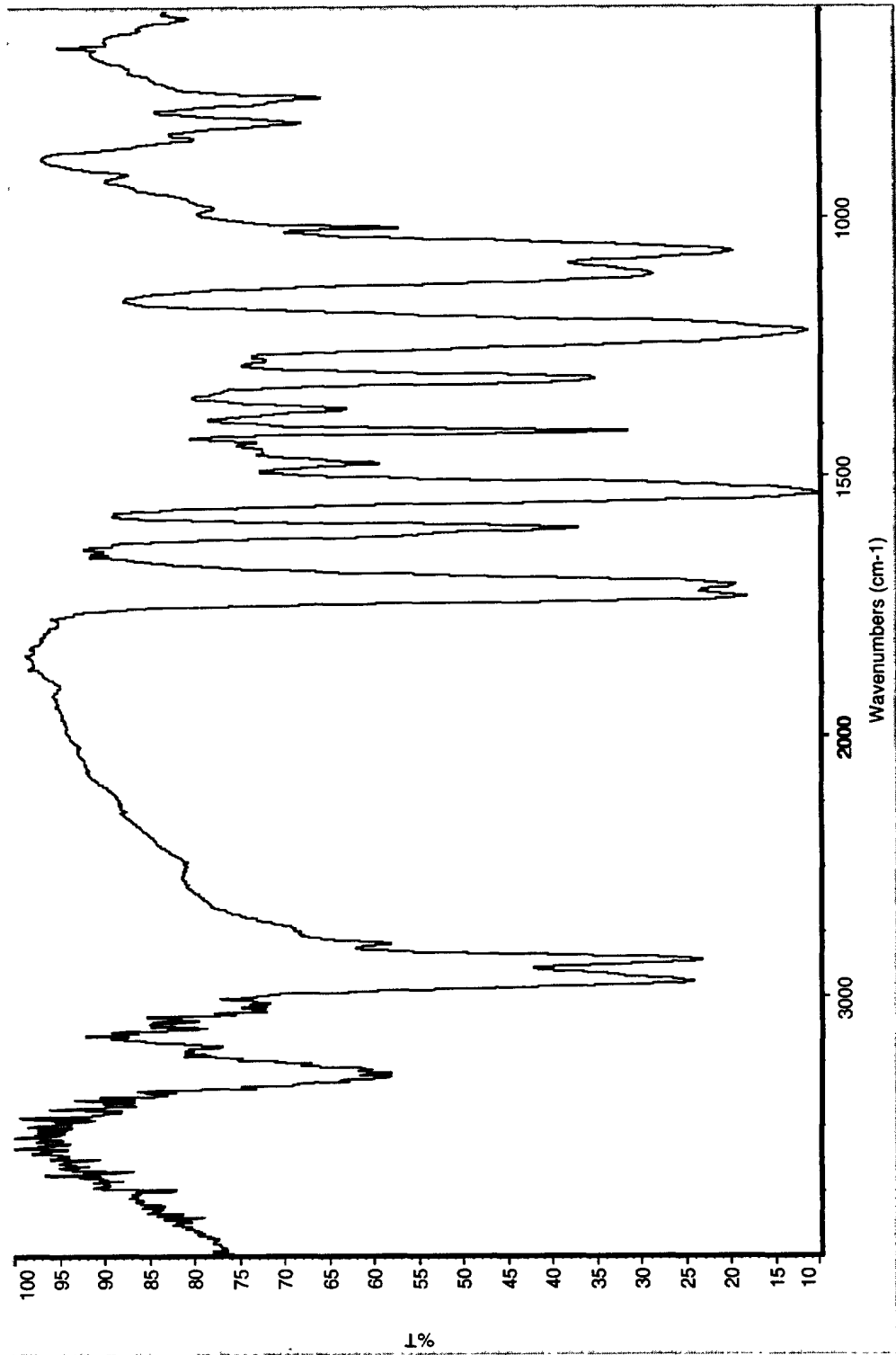


Figure 7 - Infrared spectrum of polyurethane sample #6 - T1400/DMPG/MDI (1.0/5.0/6.0).

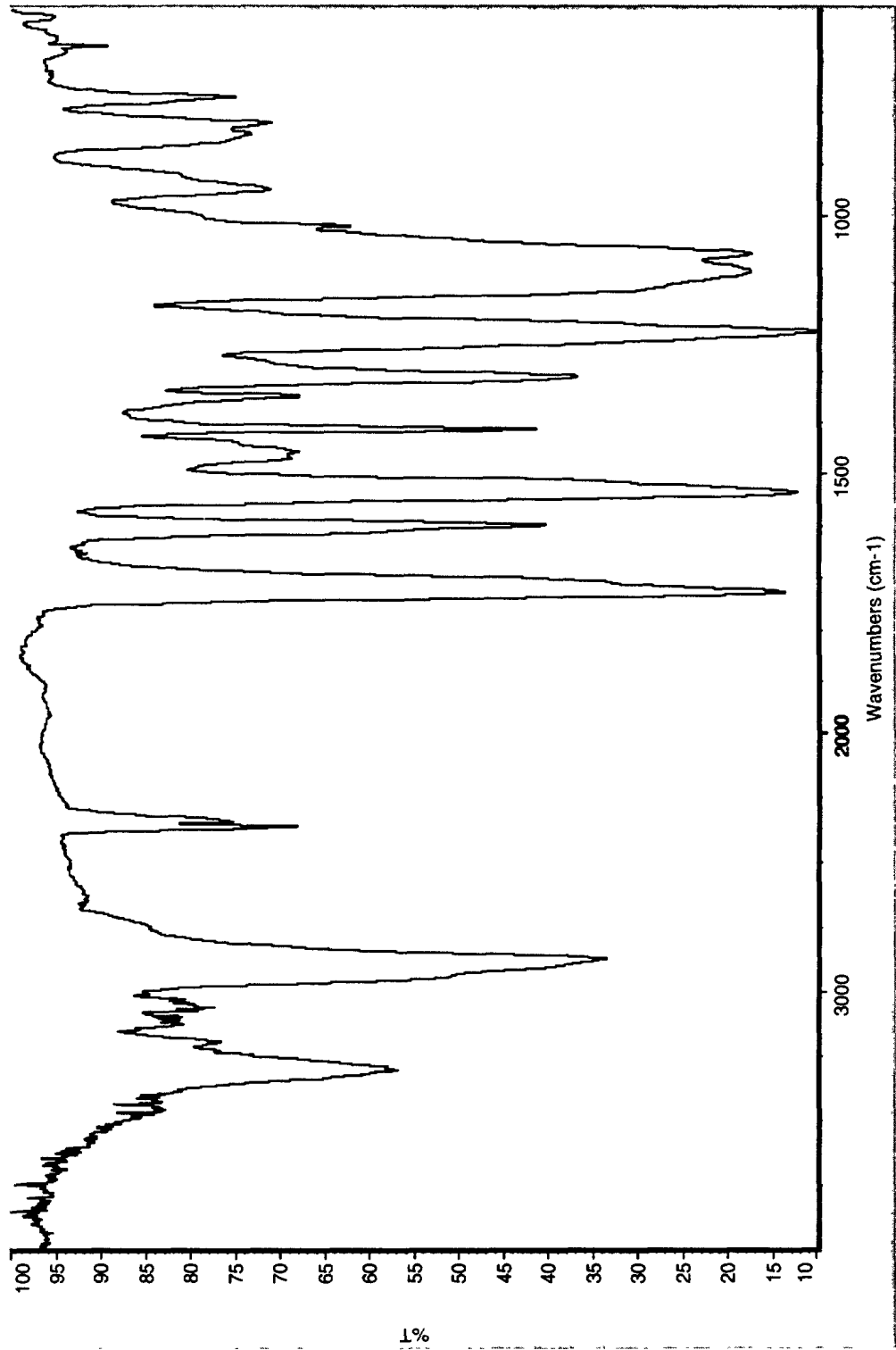


Figure 8 - Infrared spectrum of polyurethane sample #8 – P600/DMPD/MDI (1.0/0.5/1.5).

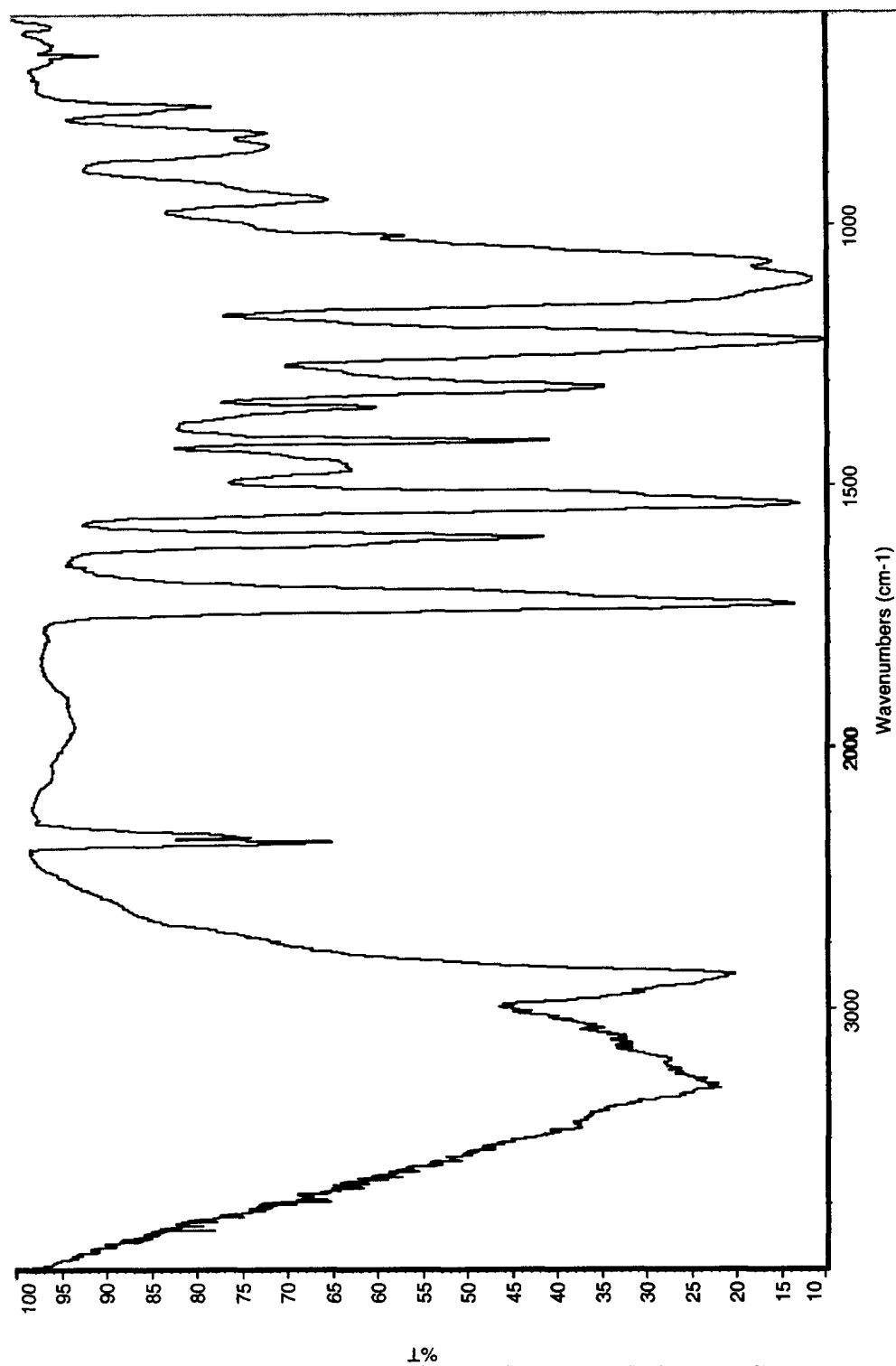


Figure 9 - Infrared spectrum of polyurethane sample #9 – P1000/DMPD/MDI (1.0/1.0/2.0).

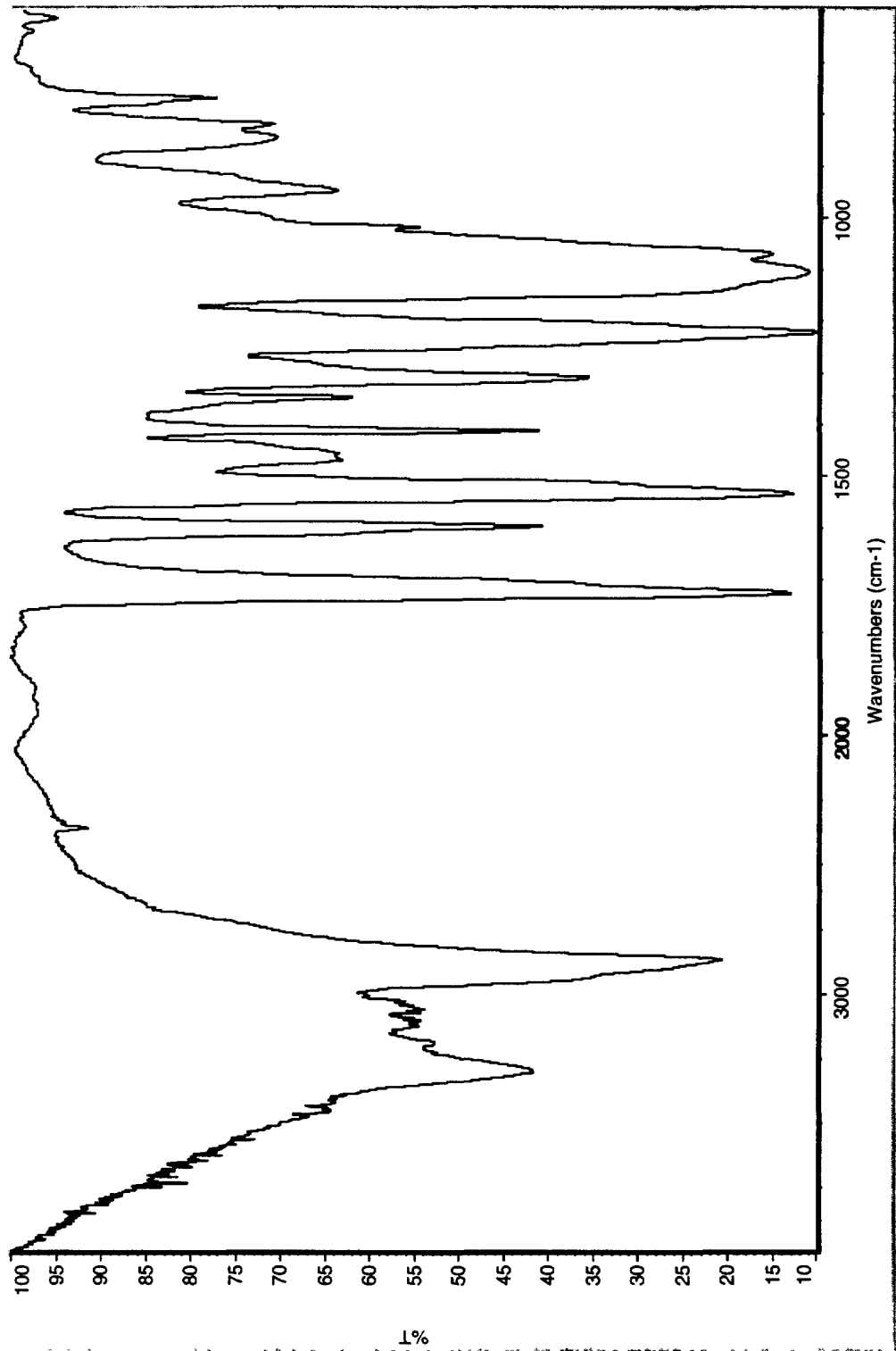


Figure 10 - Infrared spectrum of polyurethane sample #9R - P1000/DMPD/MDI (1.0/1.0/2.0).

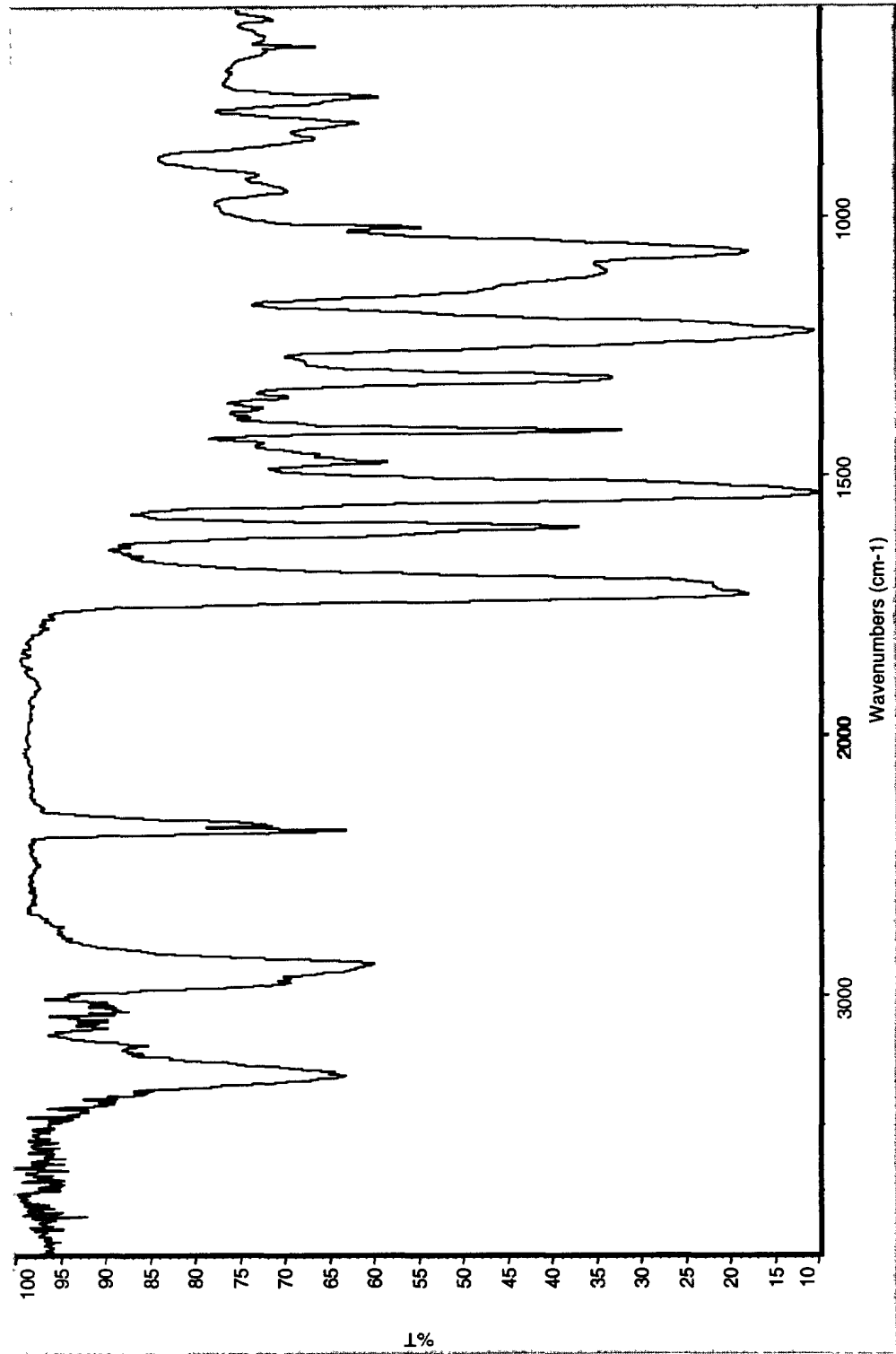


Figure 11 - Infrared spectrum of polyurethane sample #10 – P1000/DMPD/MDI (1.0/5.0/6.0).

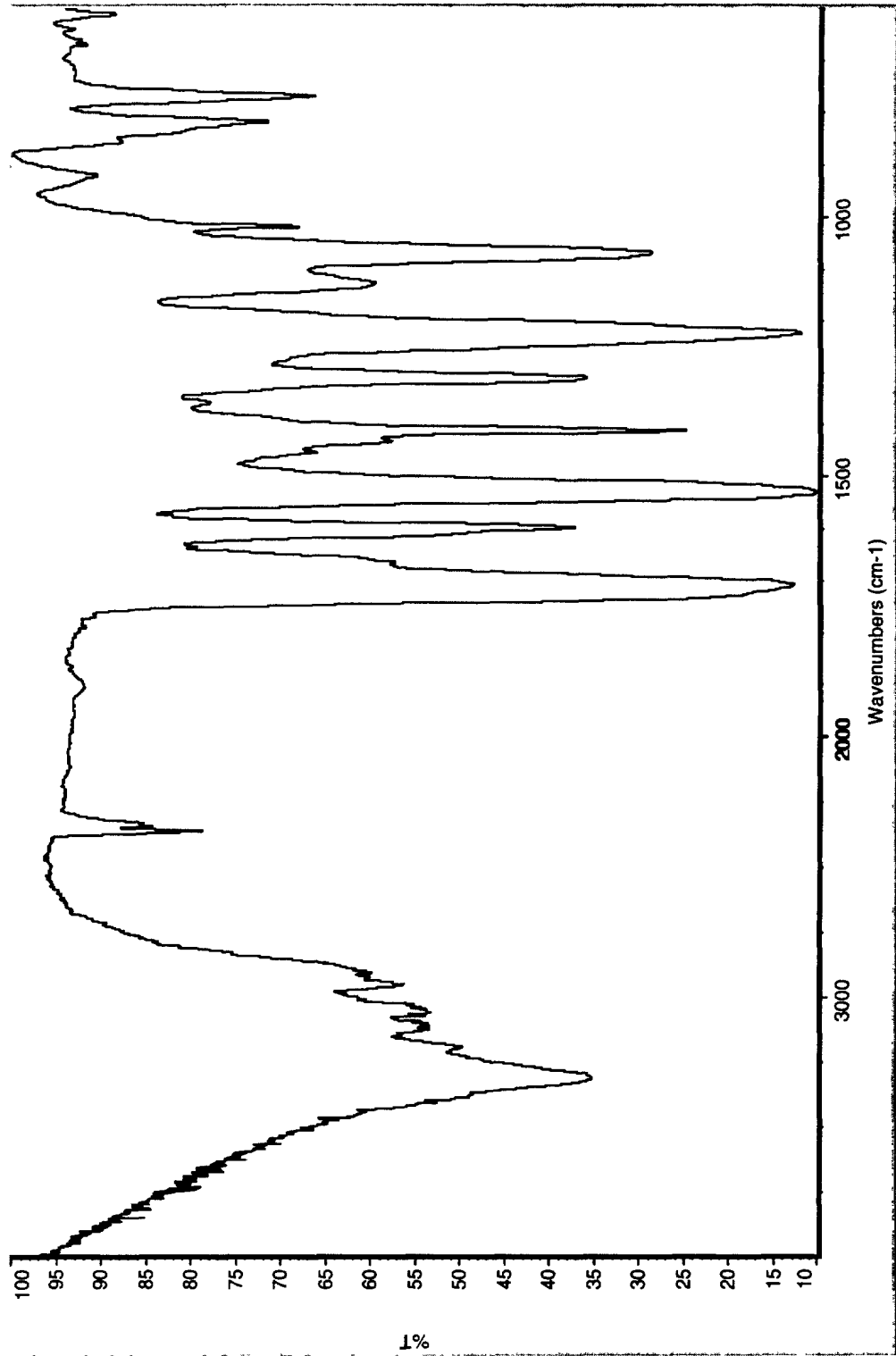


Figure 12 - Infrared spectrum of polyurethane sample #13 – DEGMDI (1.0/1.0).

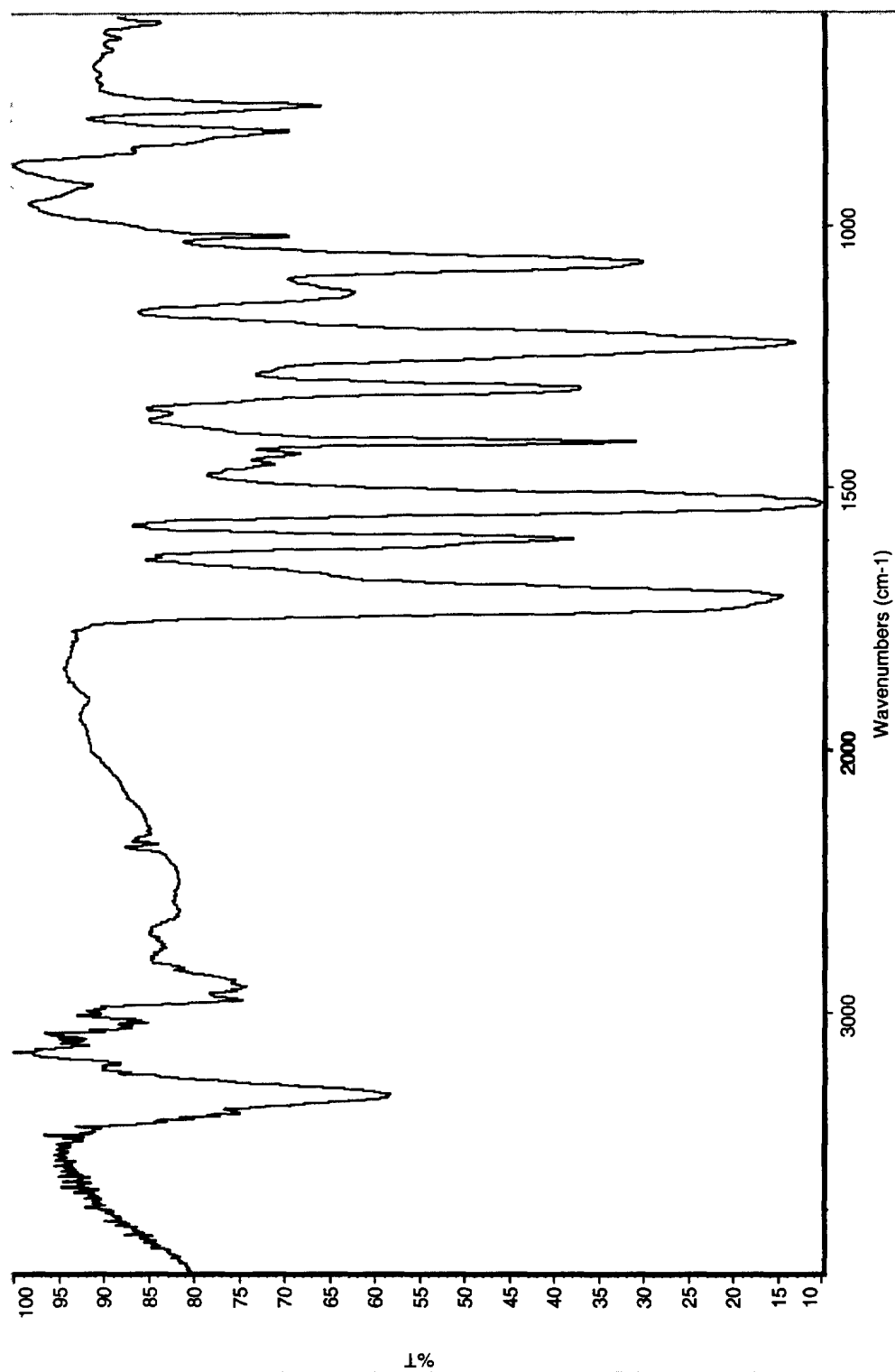


Figure 13 - Infrared spectrum of polyurethane sample #13R - DEG/MDI (1.0/1.0).

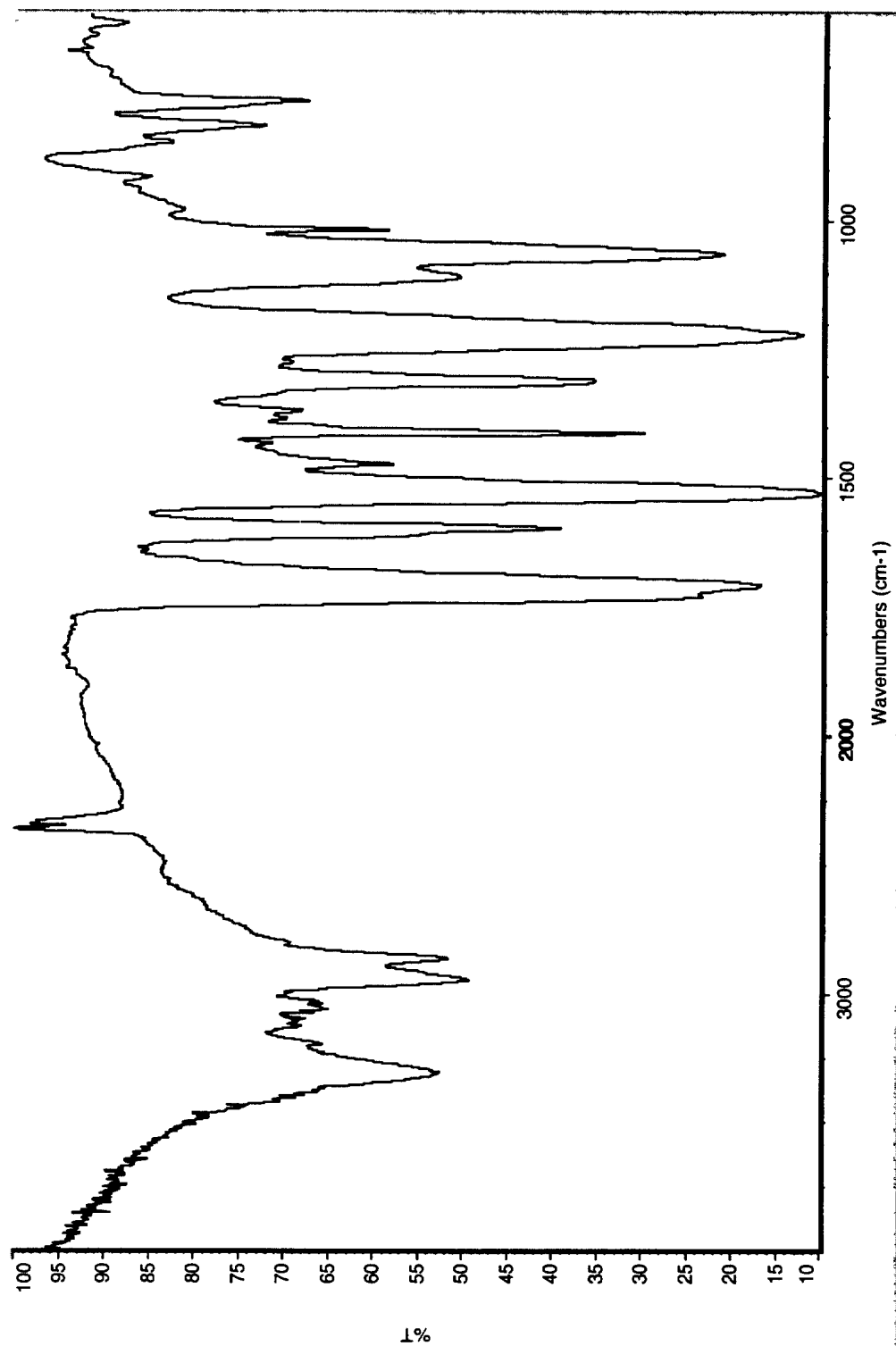


Figure 14 - Infrared spectrum of polyurethane sample #14 - T650/DMPD/MDI (1.0/5.0/6.0).

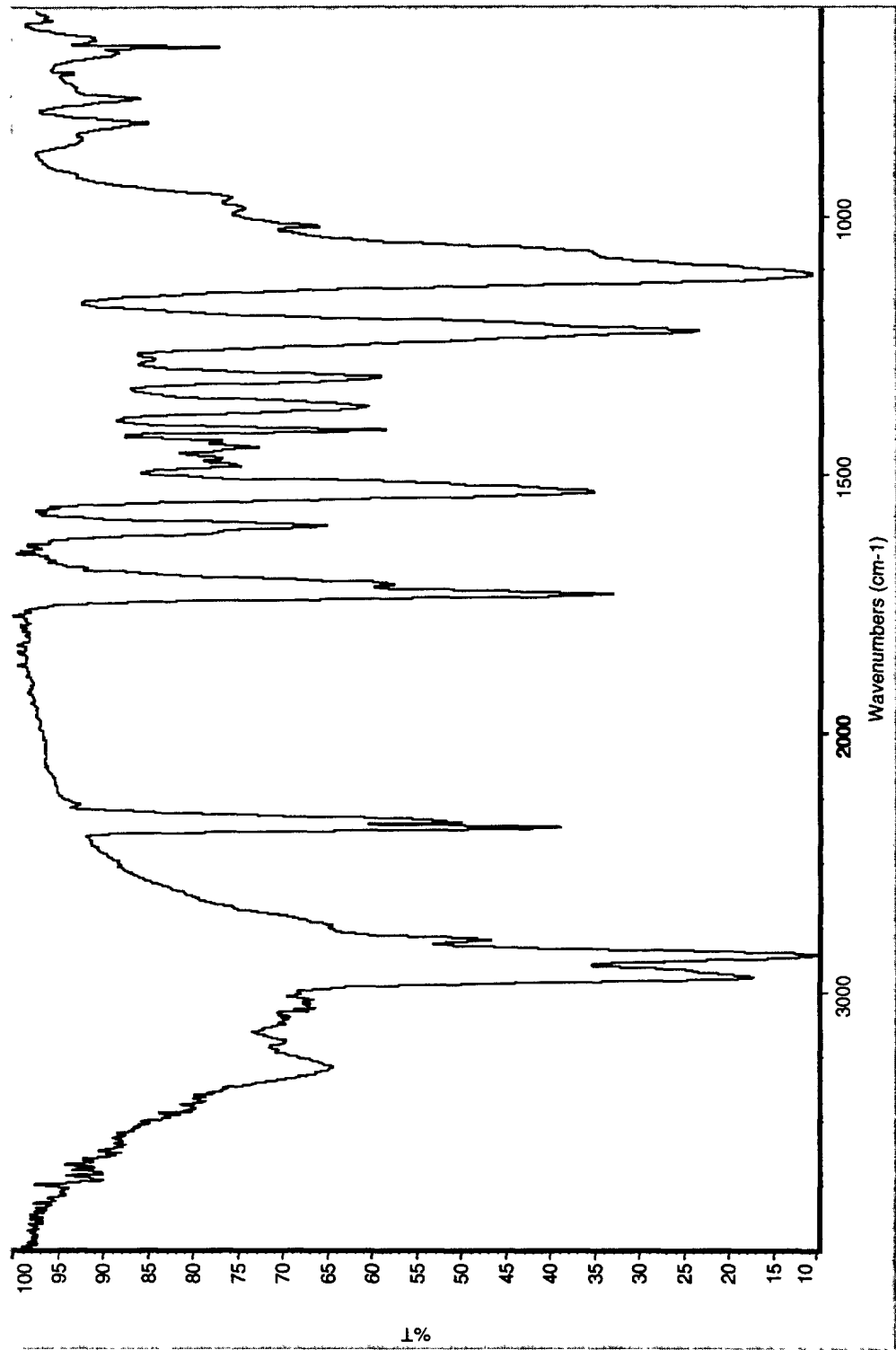


Figure 15 - Infrared spectrum of polyurethane sample #16 - T1000/MDI (1.0/1.0).

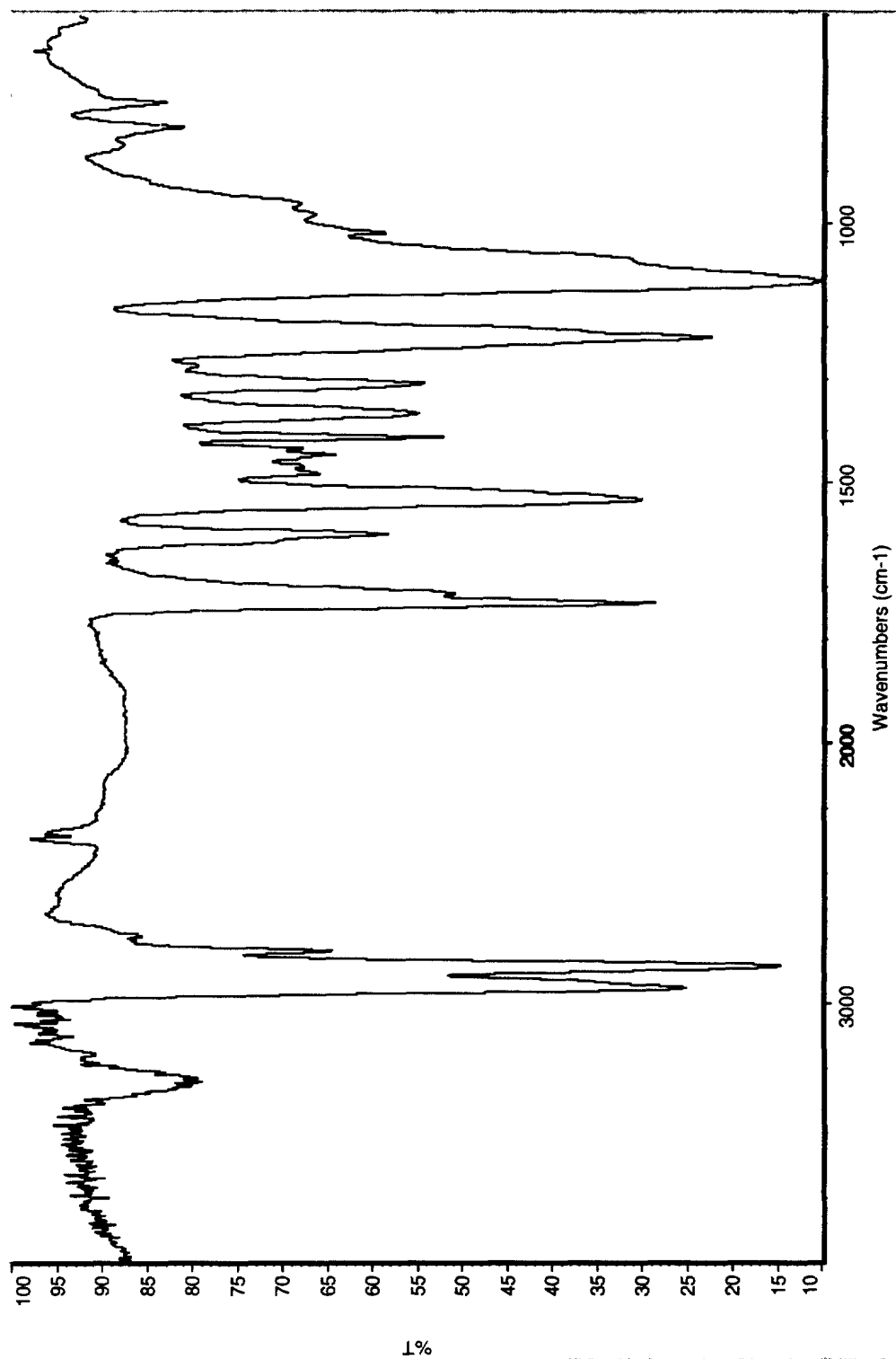


Figure 16 - Infrared spectrum of polyurethane sample #16R - T1000/MDI (1.0/1.0).

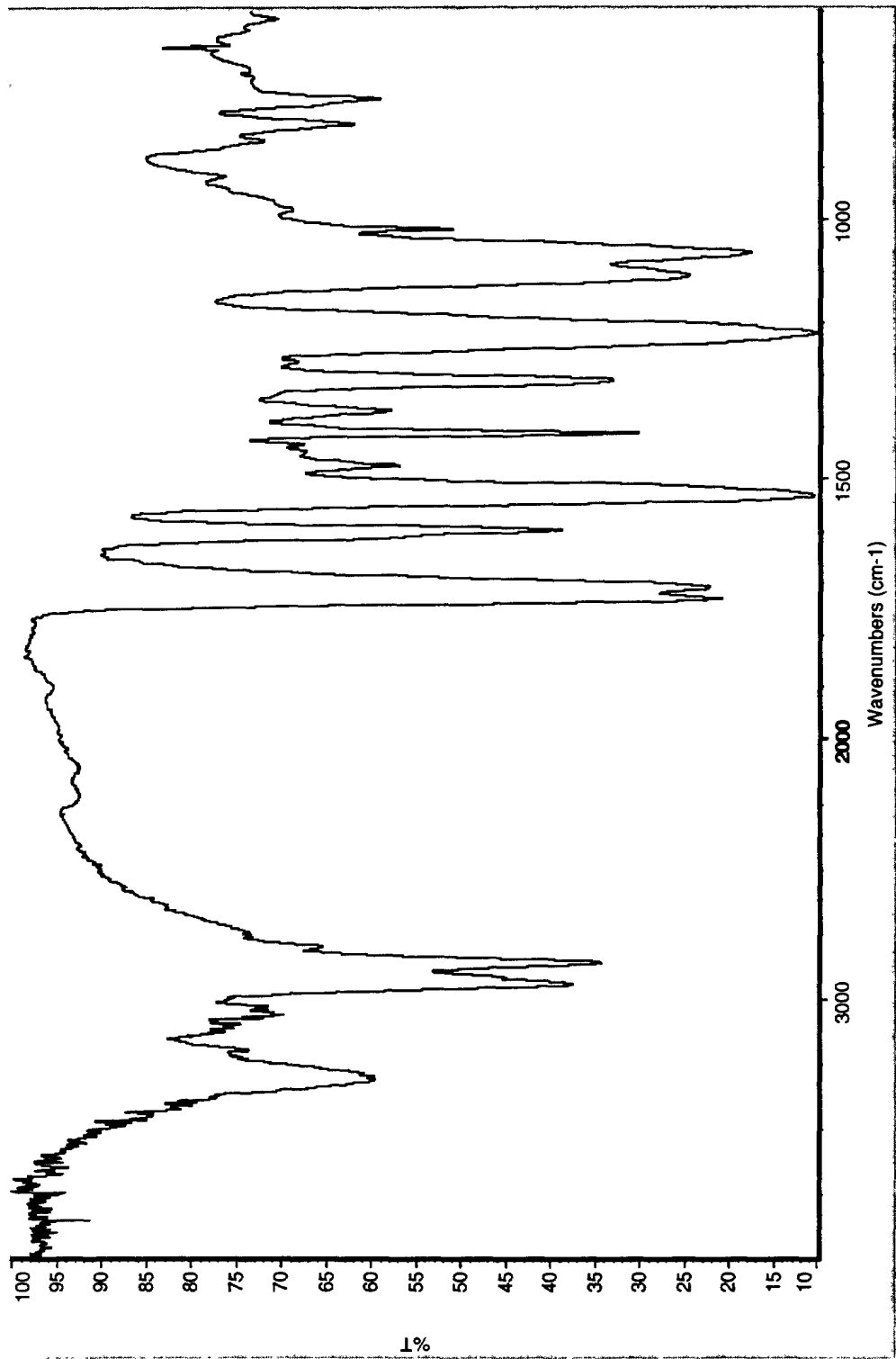


Figure 17 - Infrared spectrum of polyurethane sample #17 – T1000/DMPD/MDI (1.0/3.0/4.0).

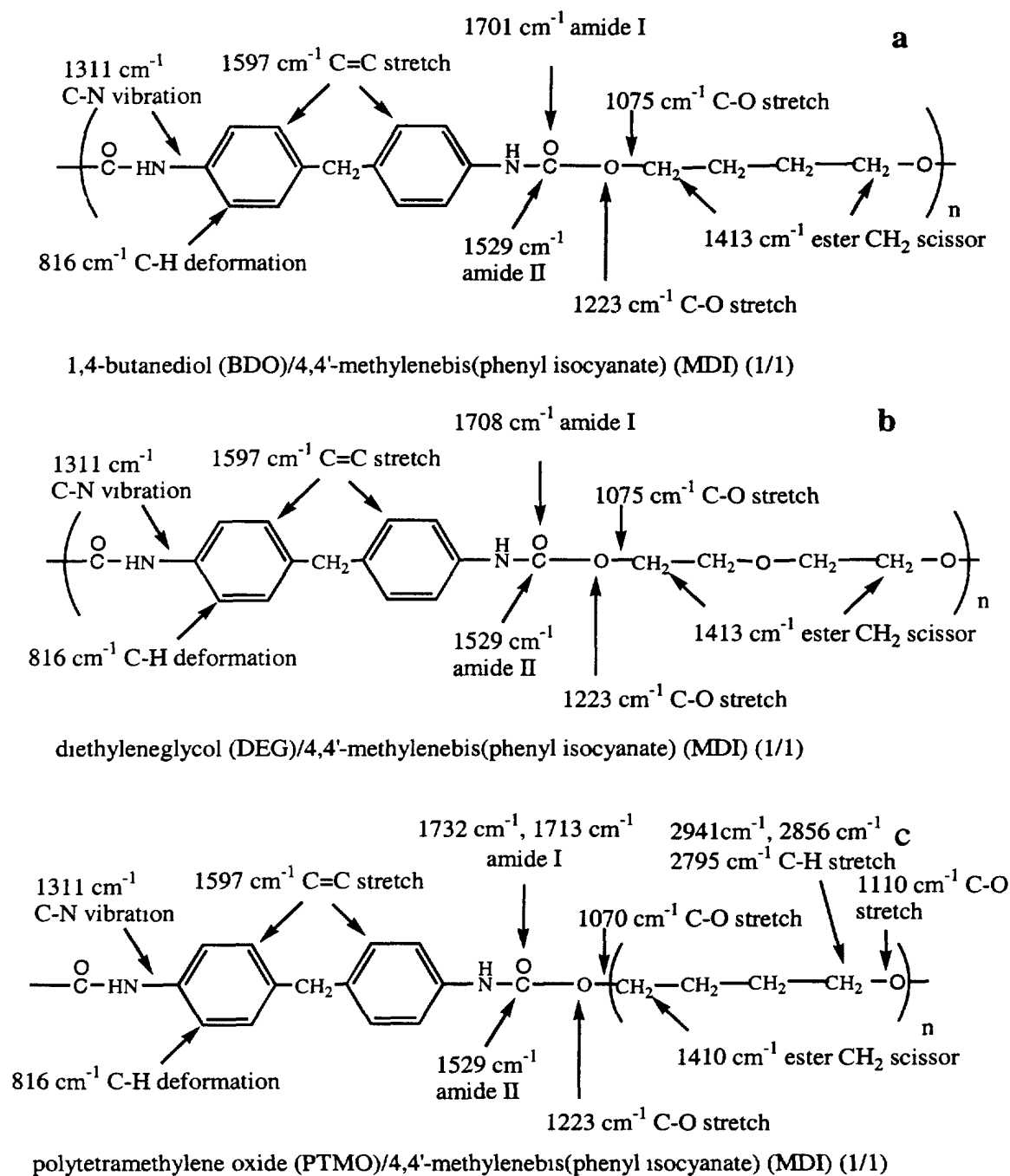


Figure 18. Assignment of IR bands of a) samples #1 and #1R, b) samples #13 and #13R, and c) samples #16 and #16R.

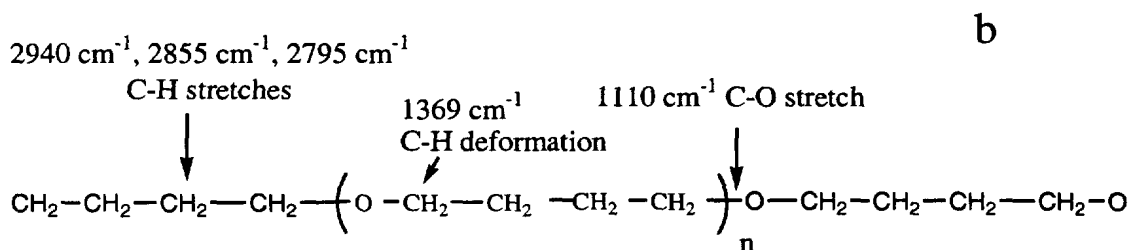
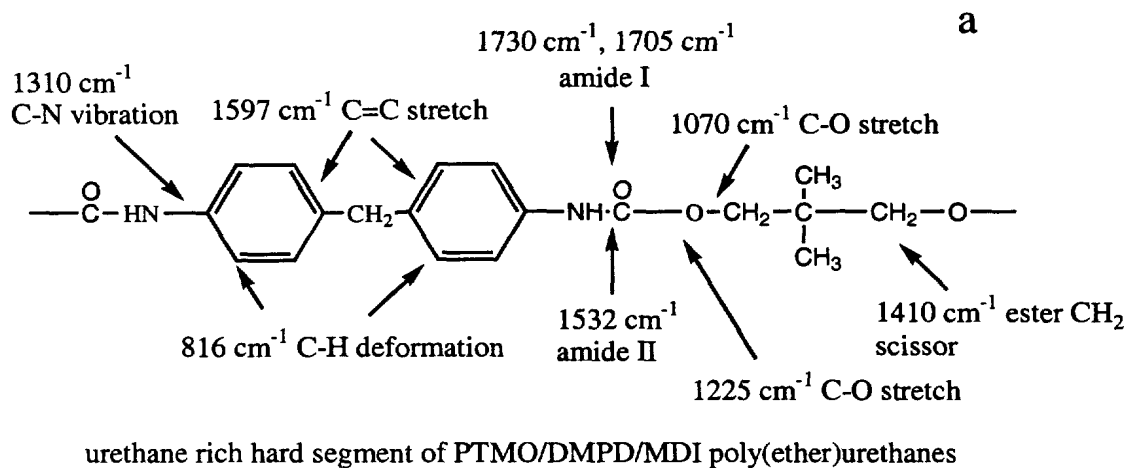


Figure 19. Assignment of IR bands of a) urethane rich hard segment and b) polytetramethylene oxide rich soft segment of PTMO/DMPD/MDI poly(ether)urethane samples #3, #4, #5, #6, #14, and #17.

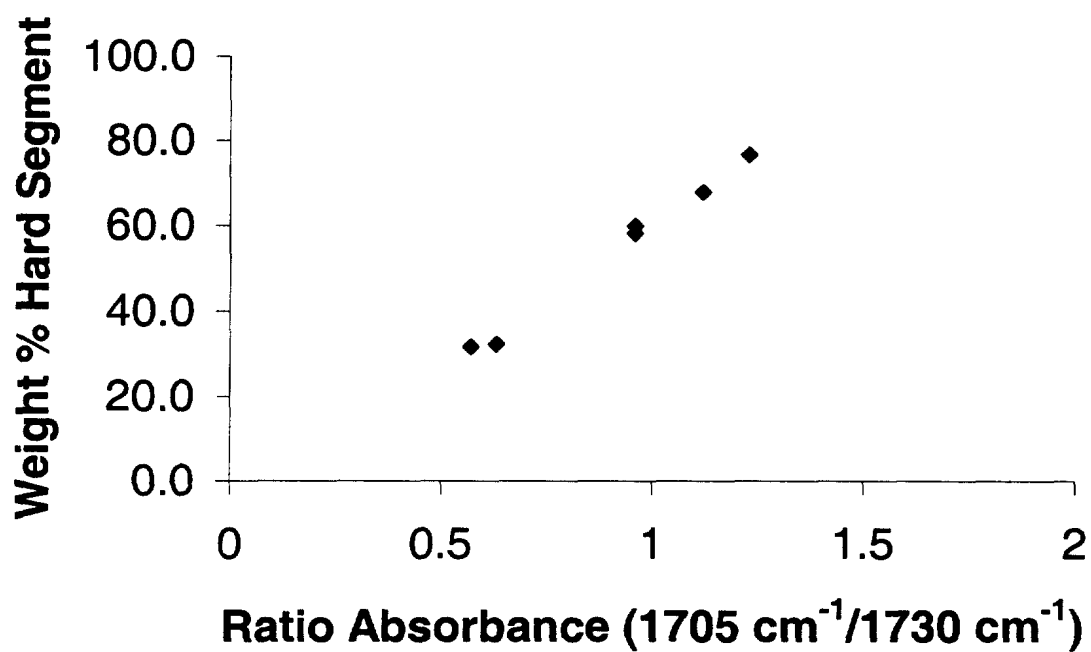
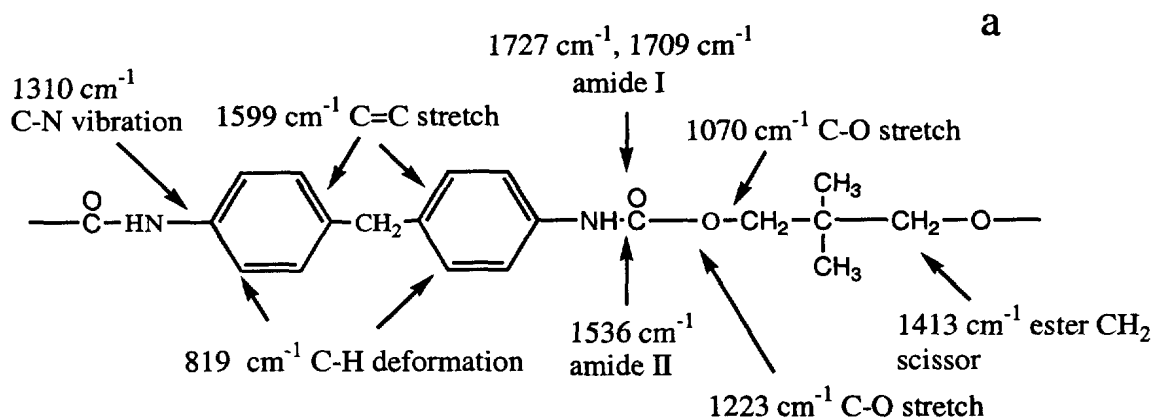
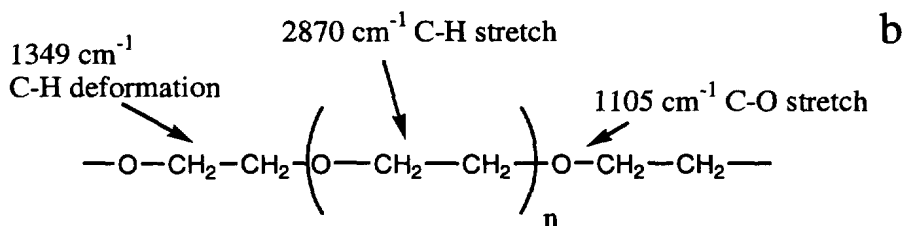


Figure 20. Plot of the ratio of the intensities of the hydrogen bonded and non hydrogen bonded amide I bands at 1705 cm⁻¹ and 1730 cm⁻¹ against weight % hard segment in poly(ether)urethanes #3, #4, #5, #6, #14, and #17.



urethane rich hard segment of PEG/DMPD/MDI poly(ether)urethanes



polyethylene glycol rich soft segment of PEG/DMPD/MDI poly(ether)urethanes

Figure 21. Assignment of IR bands of a) urethane rich hard segment and b) polyethylene glycol rich soft segment of PEG/DMPD/MDI poly(ether)urethane samples #8, #9, #9R and #10.

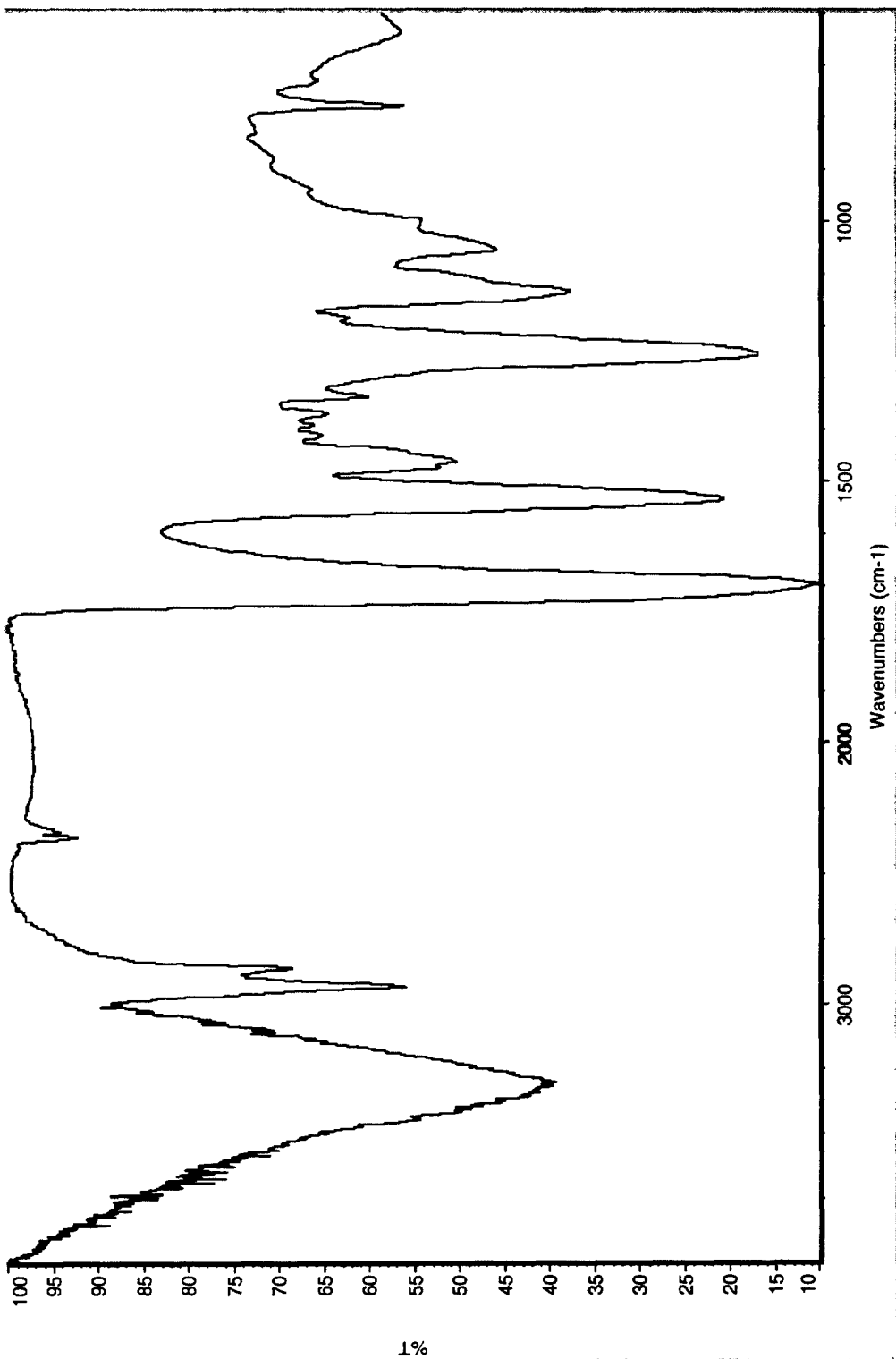


Figure 22 - Infrared spectrum of polyurethane sample #2 - BDO/DMPD/MDI (1/1/2).

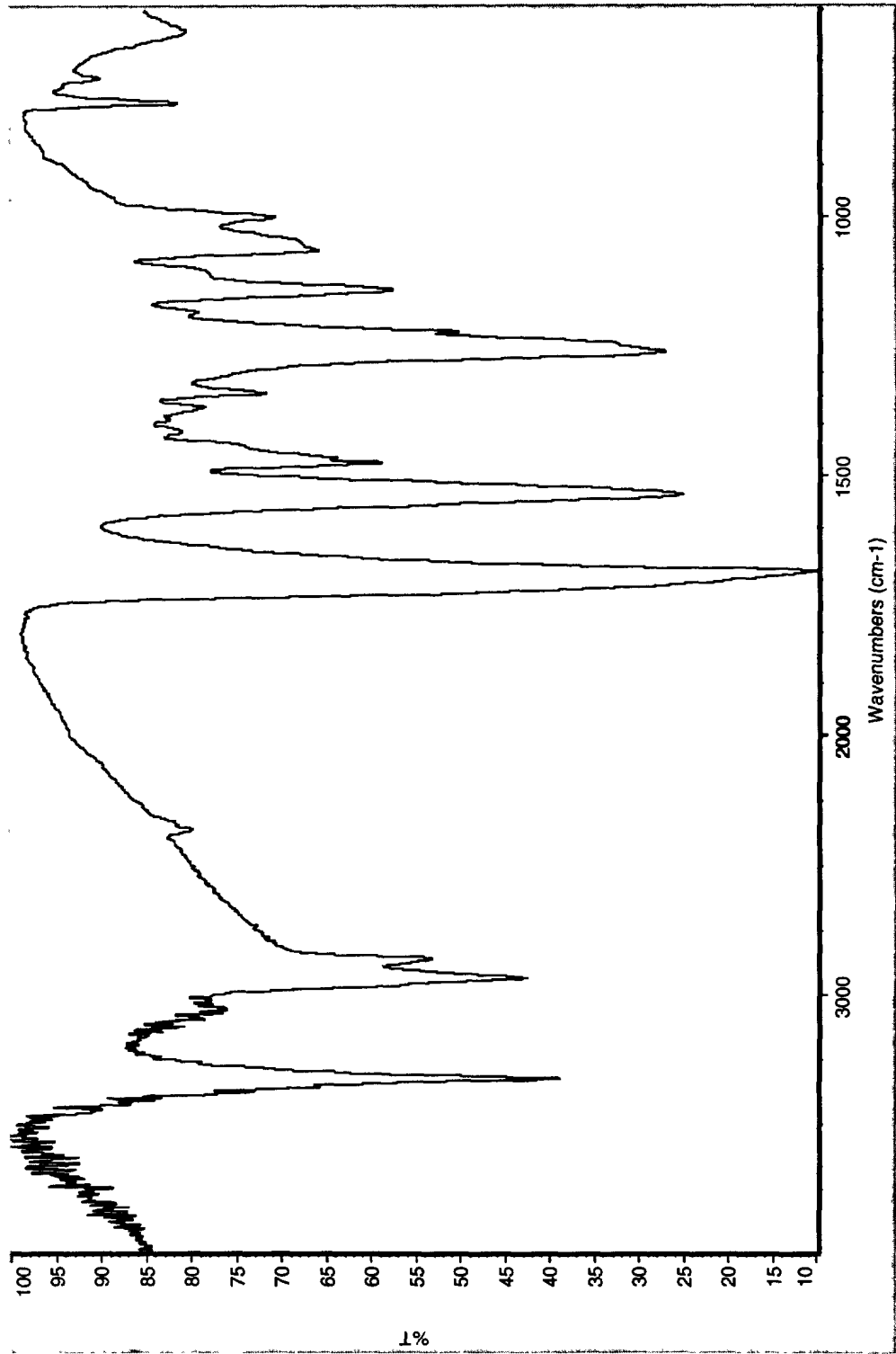


Figure 23 - Infrared spectrum of polyurethane sample #7 – DEG/DMPD/HDI (1.0/1.0/2.0).

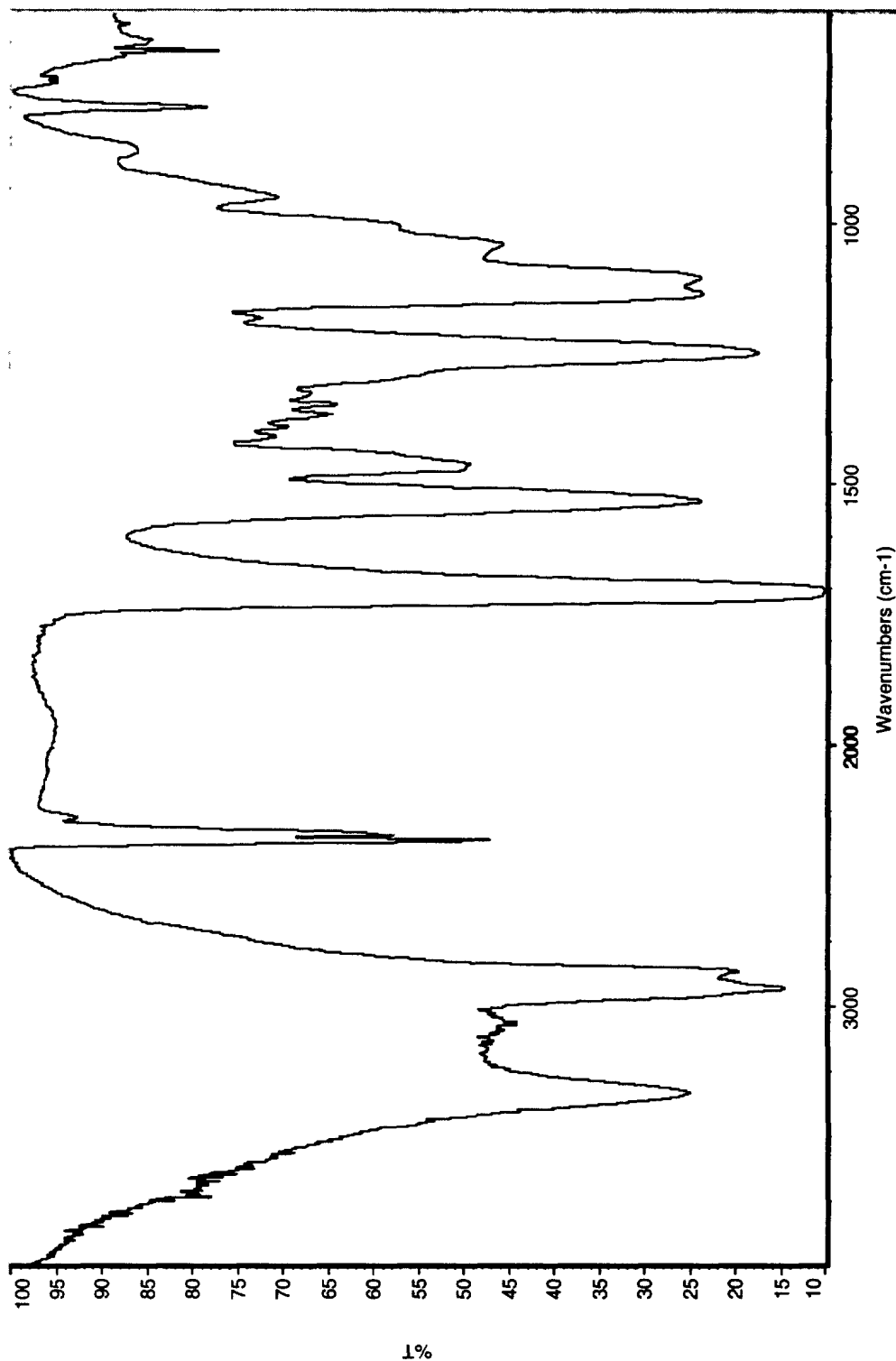


Figure 24 - Infrared spectrum of polyurethane sample #11 – P1000/DMPD/HDI (1.0/5.0/6.0).

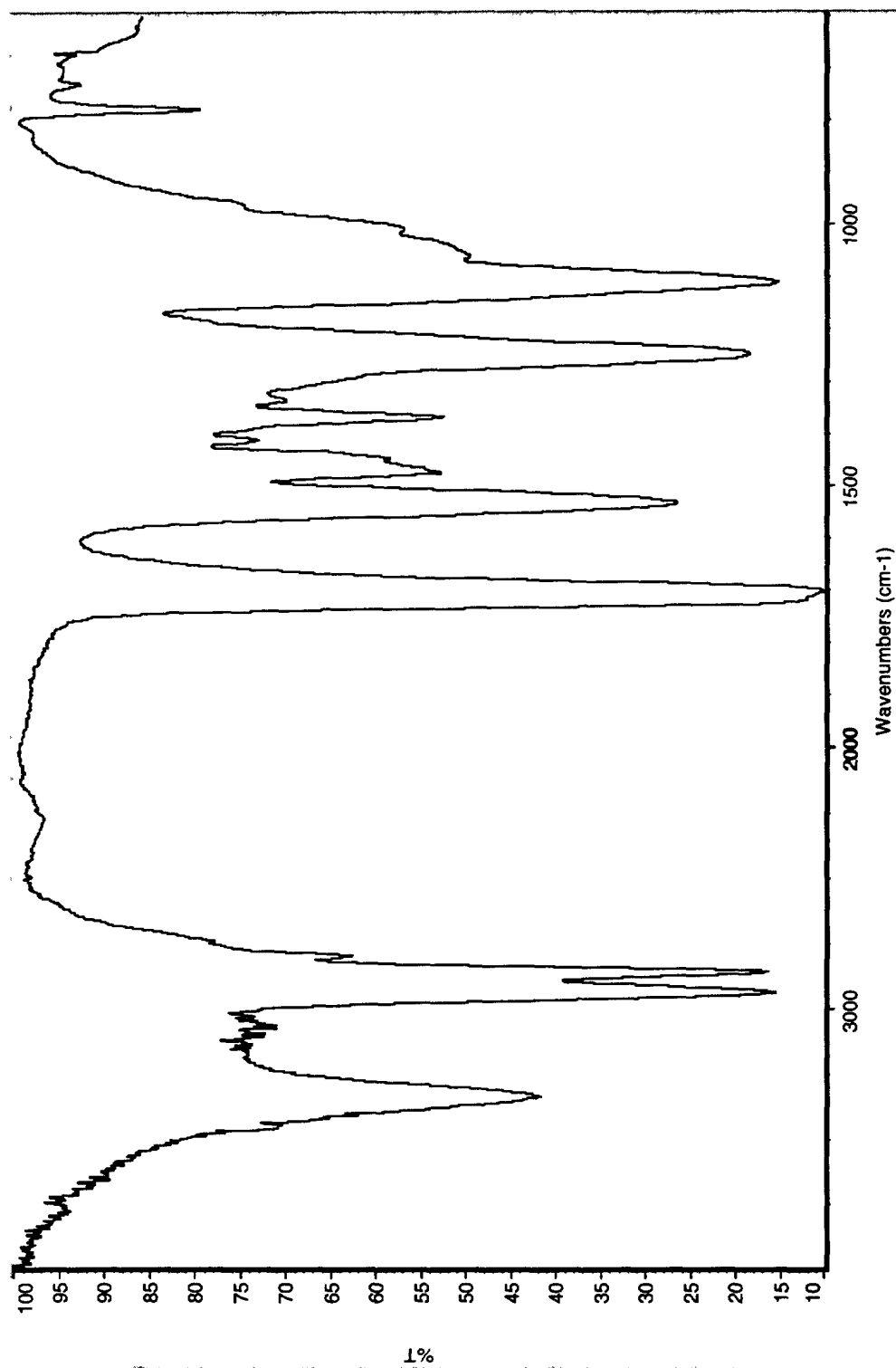
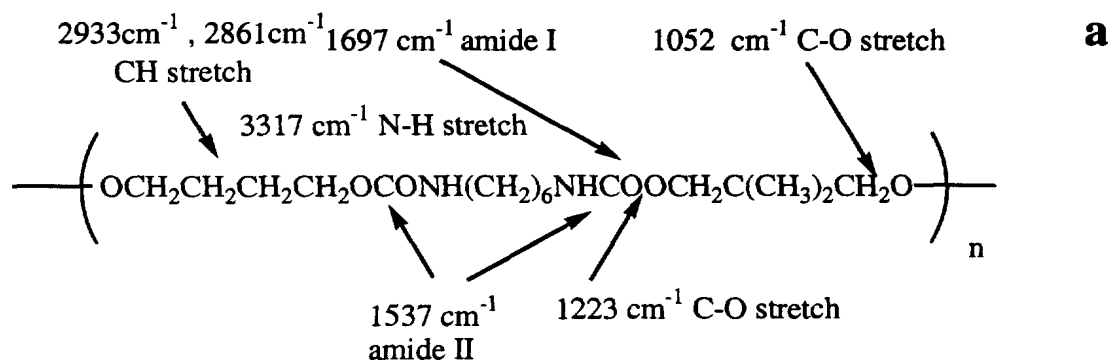


Figure 25 - Infrared spectrum of polyurethane sample #18 - T1000/DMPD/HDI (1.0/3.0/4.0).

Butanediol (BDO)/dimethylpropanediol (DMPD)/hexamethylene diisocyanate (HDI)



Diethylene glycol (DEG)/dimethylpropanediol (DMPD)/hexamethylene diisocyanate (HDI)

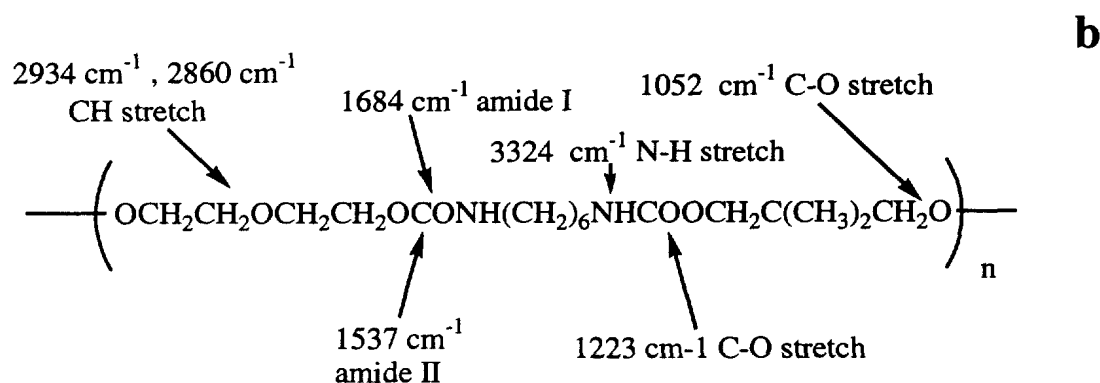


Figure 26. Assignment of IR bands of samples a)#2 and b) #7.

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The infrared (IR) spectra of sixteen 4,4'-methylenebis(phenyl isocyanate) (MDI) based and four 1,6-diisocyanatohexane (HDI) based poly(ether)urethane (AB)_n block copolymers are presented. Differences in the IR spectra of these polymers are related to differences in the diols and polyether glycols and the ratios of reactants used to synthesize them. IR spectroscopy can distinguish between the MDI and HDI poly(ether)urethanes and identify the diols and polyether glycols used to prepare the polymers. The intensity of the amide I bands (non-hydrogen bonded and hydrogen) are found to depend on the hard segment weight fraction of the polymers and are indicative of the degree of hydrogen bonding in the polymers. The relative intensity of the C-O stretches in the hard and soft segments of the polymers were found to increase with hard segment weight fraction.

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 1,6-diisocyanatohexane (HDI)
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 diethylene glycol
 1,4-butanediol

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