PROBING THE CURE AND POSTCURE REACTIONS IN POLYURETHANES BY FTIR AND GPC☆

Salehi, Hamed*
Department of Chemistry, Faculty of Science, Tarbiat Modarres University,
P.O.Box 14155-4838, Tehran, Iran.
Eslami, Mozaffar
Research Institute of Petroleum Industry, P.O.Box 18745-4391, Tehran, Iran.
Sarbolouki, Mohammad Nabi*
Institute of Biochemistry and Biophysics, Tehran University,
P.O.Box 13145-1384, Tehran, Iran.

ABSTRACT: *Fourier transform infrared (FTIR) and gel permeation chromatography (GPC) were respectively utilized in determining the changes in isocyanate (NCO) concentration and molecular weight (MW) and its distribution (MWD) in polyurethanes during their cure and postcure stages. Samples, originally cured at 45°C, were taken through accelerated aging tests at various temperatures. The FTIR and GPC analytical conditions were optimized, for both molecular weight and molecular weight distribution and NCO group determination. In FTIR spectroscopy Beer's law was obeyed over the ranges: 2.33-22.34 and 0.03-1.61 mmol lit^{-1}. RSD, detection limit and molar absorptivity were found to be 1.46%, 4×10^{-6} mol lit^{-1} and 1095 lit mol^{-1} cm^{-1} respectively. It was found the NCO concentration decreases with the progress of polymerization and at the same time MW of the sol increases, going through a maximum and then decreases to a constant level. The time to reach this level and termination of NCO concentration, i.e., the end of polymerization decreases with the increase in temperature. The results obtained from GPC and FTIR methods in following the different steps of polymerization as well as those from the linear plots of the end time of reaction vs. the 1/T, were in good agreement.*

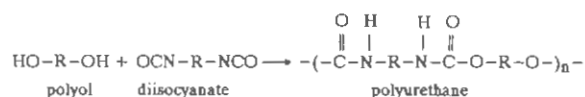**KEY WORDS:** *Polyurethane, GPC, FTIR, Cure, Postcure, Accelerated aging, NCO concentration.*

INTRODUCTION

Polyurethanes (PU) are addition polymers formed via a step growth mechanism by a reaction between a di- or poly-isocyanate and a polyol:

$$HO-R-OH + OCN-R-NCO \longrightarrow -(-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R-O-)_n-$$

polyol   diisocyanate   polyurethane

PUs are utilized in a great variety of commodities, from ships to footwear, constructions to cars, etc [1]. During the cure step the hydroxyl groups react with the isocyanate groups, leading, to a gradual decrease in their concentrations. During the advancement of polymerization molecular weight (MW) increases while the molecular weight distribution (MWD) changes cotinuously. In this paper GPC and FTIR were utilized for studying the changes in isocyanate concentration and MW and MWD of the sol during the polymerization.

EXPERIMENTAL
Materials and methods

Polypropylene glycol (PPG) and polystyrene (PS) standards were used as GPC standards. Toluene and CCl_4 were used as solvents.

Polyurethane samples were prepared by the one shot polymerization technique [2] by using PPG as the polyol and TDI as the diisocyanate with other additives [3], then they were cast and cured for 93 hours. At different intervals the polyurethanes were sampled for GPC and FTIR studies. After the cure step, the samples went through accelerated aging tests at various temperatures (25, 45, 60, 70°C) and at different time intervals, tests, were done to provide data for postcure studies.

Instruments

GPC chromatograms and FTIR spectra were obtained using the instruments of LC-4A, CR-4AX (*Shimadzu,* Kyoto, Japan) and FTIR IFS-88 (*Brucker,* Karrelsruhe, Germany) respectively.

GPC method

Since toluene has a solubility parameter near to that of the PUs [4,5] and is thus a suitable solvent [3,4]. Also it is a common solvent used in GPC [6]

and in this case gives the maximum difference with PPG in refractive index, relative to other solvents [7,8]. Hence it was selected as both the mobile phase and the solvent in these GPC studies. Sample solutions were prepared by cutting polyurethanes into thin shavings about $400\mu m$ thick and their soluble (sol) fractions was extracted with toluene in two stages followed by four toluene washes. The original extract was centrifuged and filtered by means of a Milex Filter, then injected into the GPC. After preliminary tests on the GPC columns [9], the optimum conditions were found to be as follows: Mobile phase: toluene, columns: $10^3Å$, $10^4Å$, detector: refractive index, flow rate: 1 mL min^{-1}. The mobile phase was degassed by ultrasonic vibration before using.

FTIR method

Sample preparation was similar to that of GPC save that CCl_4 was selected as the solvent. Operational conditions were as follows: liquid cell: CaF_2, detector:DTGS, pathlength: 210.5μ (pathlength determined by interference fringe technique [10]), resolution: 8 cm^{-1}, $\bar{\nu}_{max}$= 2265 cm^{-1} and triangular apodization.

RESULTS AND DISCUSSION
GPC
Calibration curves

A calibration curve was plotted by using PPG standards (MW=1200, 2000, 4000) for the low molecular weight range with -R=0.9999 (Fig. 1). PS standards were used for plotting this calibration curve both in the low MW (-R= 0.99997) and the high MW range (-R= 0.9995) [11]. In order to obtain
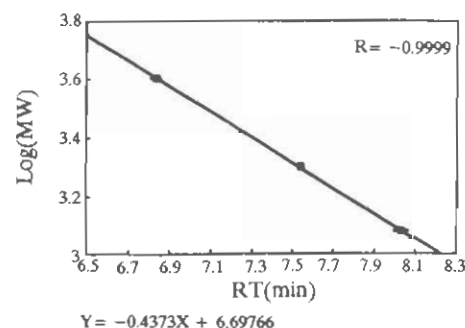

Y = −0.4373X + 6.69766

Fig. 1: GPC calibration curve (column: $10^3Å$- standards: PPG with MW's: 1200-2000-4000)
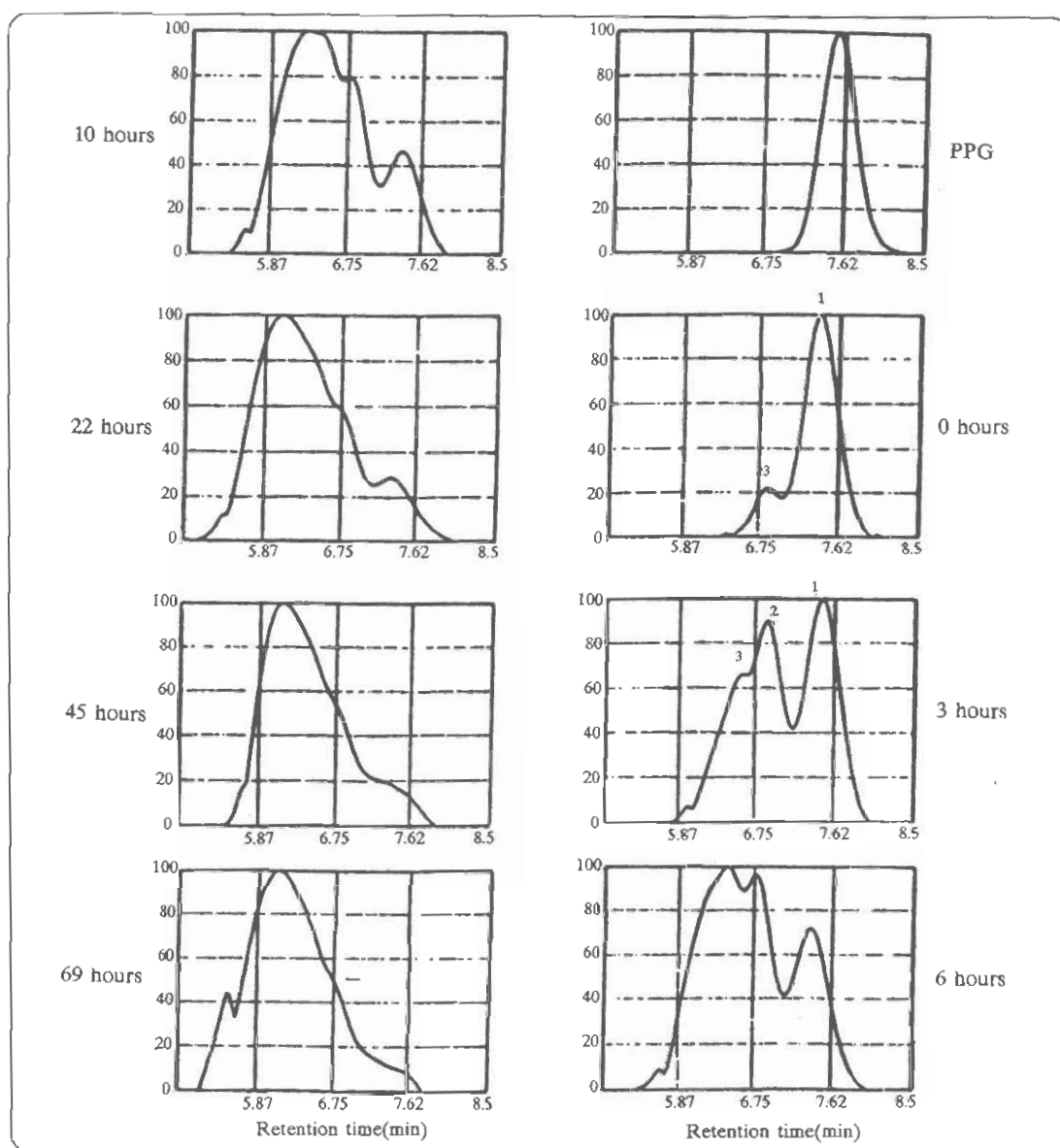
Fig. 2: GPC chromatograms during the cure stage (1) MW=2220 (2) MW=4380 (3) MW=9460

a correlation between MW that is calculated from PPG and those from PS standards, six chromatograms were analysed for the interrelation between the MW's. The relation found was: $Q=MW(PPG)/MW(PS)= 0.70$ (Table 1).

Cure stage

GPC chromatograms during the cure stage are shown in Fig. 2. At time zero (after mixing) there are two peaks, peak (1) with $MW=2220$, this means that during mixing (30 minutes) most of PPG monomer has reacted at least with one TDI molecule. The existance of peak (2) with $MW=4380$, shows that there are two PPG monomers in some polymer chains. After 3 hours of curing a new peak appeared with $MW= 9460$, this means that some of polymer chains have four PPG monomers present in this step. Gradually the MW from peak (1) and then peak (2)

Table 1: *Calculation of Q coefficient (refer to text)*

Samples	MW(PS)	MW(PPG)	Q=MW(PPG)/MW(PS)
1	3952	2820	0.71
2	4088	2906	0.71
3	4241	2986	0.70
4	4318	3040	0.70
5	4398	3089	0.70
6(PPG-4000)	5096	3992	0.68
Average	–	–	0.70

decreases, however the MW from peak (3) increases shuch that the total average MW(MW-t) increases as the polymerization proceeds. Changes of MWD (three peaks (1), (2), (3)) and MW-t vs. time are plotted in Fig. 3. It is found that the MW of the sol increases with the progress in polymerization, going through a maximum and then decreases to a constant level (MW about 15000).
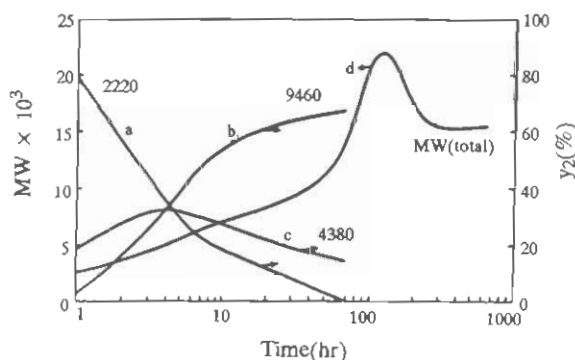

Fig. 3: *MW and MWD changes during the cure stage*
a) *Changes in MW=2220 (peak 1)*
b) *Changes in MW=9460 (peak 2)*
c) *Changes in MW=4380 (peak 3)*
y_2 *is related to a,b and c*

Similar changes have been reported [12,13] with different polymers. Probably this behaviour is due to the joining of high MW chains to crosslinked polymer (gel) or reaction of high MW chains to each other with subsequent gelation.

Postcure stage

The MW changes after each cure step at different temperatures were plotted vs. time (Fig. 4). At all temperature MW increases, and continuous through-

out the postcure stage meaning that polymerization is not completed in the cure stage. After going a maximum, MW, decreases to a constant level. The time to reach this level, considered to be the end of polymerization, decreases with increasing temperature. These times for 25, 45, 60 and 70°C are 38, 8, 5 and 2 days respectively.
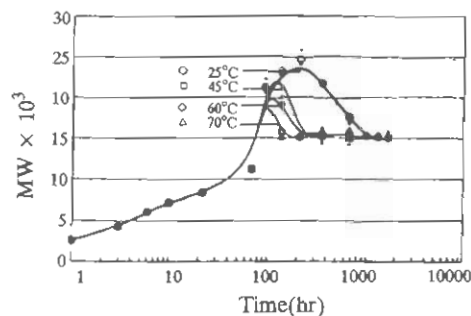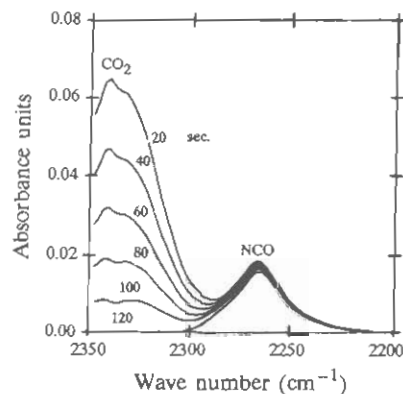

Fig. 4: *MW changes during the postcure at different temperatures*

FTIR
Elimination of the CO_2 interference band

The isocyanate group has a $\lambda_{max}= 2265$ cm^{-1} in the IR that interferes with the CO_2 band (Fig. 5). To eliminate this interference, of a N_2 gas was applied, then it was found that after two minutes the CO_2 peak is eliminated.

Fig. 5: *Elimination of CO_2 peak by purging of N_2 gas*

Calibration curves and study of beer's law

A calibration curve for NCO was plotted over the range 2.23-22.34 mmol lit^{-1} (R= 0.9999) and the average molar absorbtivity, detection limit and RSD for 11 measurments were found to be 1095 lit mol^{-1}

cm^{-1}, 4 E-6 mol lit^{-1} and 1.4% respectively. Inter-
ference of the polymer additives in quantitative ana-
lysis of NCO was studied (Fig. 6); no interference
was found to occur. With the progress of polymeri-
zation, NCO concentration obviously decreases, there-
fore a second calibration graph was plotted for low
concentrations, with increasing pathlength from 210.5
to 1070μ in the range 0.03-1.61 mmol lit^{-1} (R=
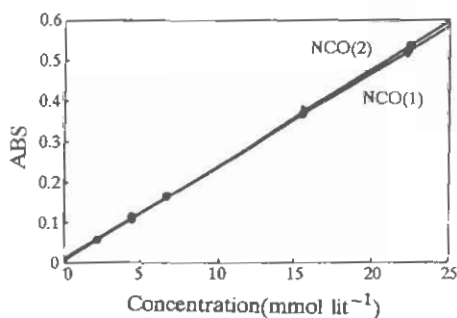0.9998).

Fig. 6: Study of additive materials interference in quantitative analysis of NCO
NCO(1): Calibration curve from pure TDI
NCO(2): Calibration curve from TDI+additive materials

Cure stage

FTIR spectra and NCO concentration during the
cure time are shown in Figs. 7 and 8 respectively. It
is found that the NCO concentration decreases to
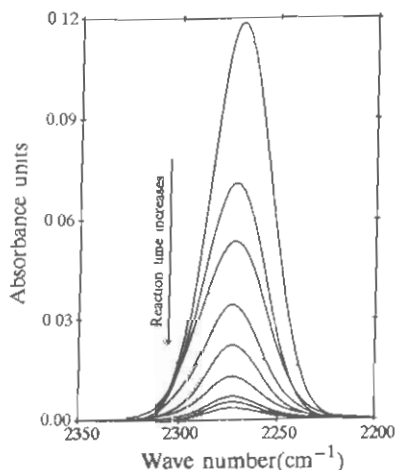less than 1/2 of its initial value during the mixing
time.

Fig. 7: FTIR spectra during the cure stage showing the reduc-
tion in NCO group concentration as reaction time increases: 0,
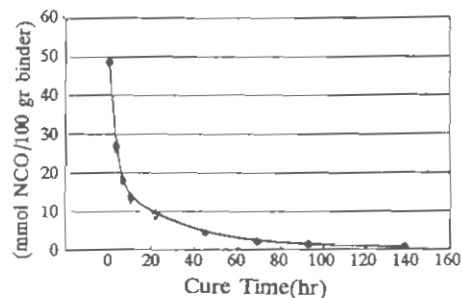*3, 6, 10, 22, 40, 69, 93, 139 hours.*

Fig. 8: NCO changes during the cure stage (45°C) (initial
value of NCO is 104.09 mmol/100 gr binder)

Postcure stage

FTIR spectra at different temperatures were
obtained and changes of NCO concentration were
plotted vs. the time (Fig. 9). It was found the
polymerization is not completed in the cure stage.
Similar results were found from GPC measurements
of the postcure stage. The time to obtain NCO
termination is considered to mark the end of poly-
merization and decreases with the increase in tempe-
rature. These times for 25, 45, 60 and 70°C are 38,
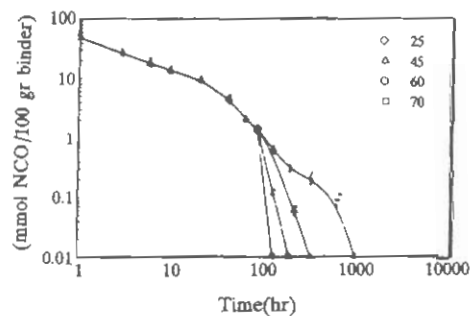11, 5 and 2 days respectively.

Fig. 9: NCO changes during the postcure at different tempera-
tures.

The correlation between the polymerization time
(t_e) and temperature was studied. Log(t_e) vs. 1/T was
plotted (Fig. 10) for data obtained from both FTIR
and GPC methods. A good linear relationship bet-
ween (t_e) and temperature was found, showing an
type Arrhenius correlation and a satisfactory agree-
ment between the two methods.

CONCLUSIONS

For the same retention time, the ratio of molecu-

lar weight of PPG to molecular weight of polystyrene (PS) found was: 0.7. For PPG and PS having the same MW's, the size (or hydrodynamic volume) of PS is found to be smaller than PPG. The isocyanate content of TDI is obtainable by FTIR. The molar absorbtivity, detection limit and RSD were found to be 1095 lit mol^{-1} cm^{-1}, 4×10^{-6} mol lit^{-1} and 1.46%, respectively. One can detect and measure through the FTIR and GPC results, the existance of the postcure stage. During this stage a good linear relation is found between both methods, between the end of polymerization and temperature, showing an Arrhenius correlation, and as well a satisfactory agreement between the two methods.
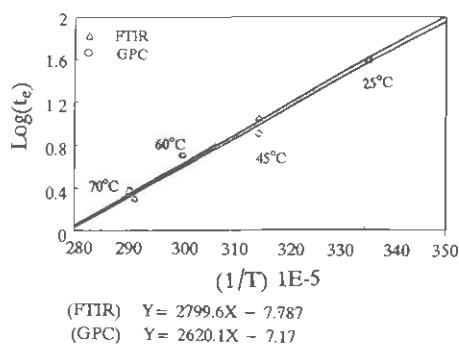

(FTIR)   Y = 2799.6X − 7.787
(GPC)   Y = 2620.1X − 7.17

Fig. 10: Correlation between time of polymerization and 1/T from GPC and FTIR methods

ACKNOWLEDGMENT

REFERENCES

[1] Woods, G., *"ICI Polyurethane Book"*. John Wiley & Sons, New York, pp. 1-6 (1987).

[2] Hepburn, C., *"Polyurethane Elastomers"*, Applied Science Publishers, London, pp. 7 (1992).

[3] Salehi, H., *"Master Thesis"*, Tehran University, Tehran, pp. 52, 115(1992).

[4] Barikani, M. and Hepburn, C., *Iranian J. of Poly. Sci. & Tech.*, 1(1), (1992).

[5] Riddick, J. A., Bunger, B. W. and Sakans, K. T., *"Organic Solvents"*, John Wiley & Sons, New York, pp. 137-8 (1987).

[6] Yau, W. W., Kirkland, J. J. and Bly, D. D., *"Modern Size Exclusion Liquid Chromatography"*, John Wiley, New York, pp. 250-1 (1979).

[7] Gaylord, G. N., *"Polyethers-part 1"*, Interscience Publishers, New York, pp. 223(1963).

[8] Hawley, G., *"Condensed Chemical Dictionary"*, Van Nostrand Reinhold, New York, pp. 1030 (1981).

[9] Salehi, H. and Paiinshahri, A., *Iranian J. of Poly. Sci. & Tech.*, 3(2) (Persian Edition) (1990).

[10] Skoog, D. A., *"Principle of Instrumental Analysis"*, Saunders College Publishing, Philadelphia, pp. 340-1 (1985).

[11] *"Waters Sourcebook for Chromatography Columns & Supplies"*, Millipore, Corporation, New England, USA, pp. 53(1987).

[12] Layton, L. H., *National Technical Information Service*, Wash. D.C., AD-A-002386(1974).

[13] Layton, L. H., *National Technical Information Service*, Wash. D.C., AD-A-010371 (1975).

[14] *"Annual Book of ASTM Standards"*, Vol. 14-01, E 168-67, American Society for Testing and Materials, Easton (1987).

[15] Rosato, D. V. and Schwartz, R. T., *"Environmental Effects on Polymer Materials"*, 1 , Interscience Publisher, New York, pp. 1172 (1968).