Polymer Bulletin

Microwave Assisted "Split-phase" Glycolysis of Polyurethane Flexible Foam Wastes

Mir Mohammad Alavi Nikje[1] (✉), Mahin Nikrah[1], Moslem Haghshenas [2]

[1]Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran
[2]Polymer & Chemistry Laboratory, ERI, 16 Km Old Karaj Road, Tehran, Iran

E-mail: alavim2006@yahoo.com; Fax: +98 281 3780040

Summary

Microwave assisted glycolysis of polyurethane (PU) flexible foam wastes at atmospheric pressure in "split-phase" condition is reported. Glycerin, sodium and potassium hydroxides were used as glycolysing agent and catalysts, respectively. Decomposition and dissolution of the foam was studied in different reaction condition. Results showed successful polyol recovering in short reaction time in comparison with conventional heating method. Finally, the recycled polyol was identified by FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopy methods, being compared with virgin one.

Keywords

Microwave; Glycerin; Polyurethane waste; Flexible PU foam; "Split-Phase"

Introduction

Many researchers have dedicated considerable effort to finding alternative methods for recovering and disposing of PU scraps [1]. Among various methods, chemical recycling which lead to polyol recovery including hydrolysis [2-4], aminolysis [5,6], glycolysis [7,8] and hydroglycolysis [9], is more interesting.
The glycolysis process has been accomplished by treatment of PU with mono-, di- and triethanolamine [10,11], ethylene glycol (EG) [12], diethylene glycol (DEG) [13,14], as well as 1,4-butanediol [15].
Today numerous applications in material processing techniques have been introduced which have resulted in shorter reaction times and greater convenience. Microwave (MW) heating offers increasing in reaction rates and reduction in electrical consumption, compared to thermal heating, as observed in several organic reactions [16, 17].
In MW assisted reactions, the efficiency of converting electrical energy to thermal energy is over 85 % and the rate of heating is faster than thermal heating [18]. In other

words, the reaction rate is increased in microwave conditions due to better heat transferring rate in comparison with conventional heating methods [19]. In addition, the results have showed the dependence of accelerated rates to various parameters such reactant-solvent ratio, microwave power, volume of reaction mixture and geometry of the vessel [20, 21].

The microwave heating effect arises when polarizable molecules tend to reorient and align themselves in an applied microwave field. The conversion of microwave energy to thermal energy depends on the dielectric constant and dielectric loss of materials. Significant effects are observed in material with high dielectric constant at a given microwave frequency and power [22, 23]. The heating effect by microwave irradiation is unique because heat is generated internally within the material. Therefore, heating phenomenon begins from inside of the materials. Also it has been found that microwave heating does not alter the composition of products appreciably when compared to those produced by conventional heating techniques [20].

MW irradiation enhances reaction rates and increases yields by limiting side reactions [24]. While some believe that these results can be explained through thermal influences, others argue that additional nonthermal or specific MW effects are at work. The exact source of MW enhancement is the subject of much controversy [25-29]. There are some reports in polymer chain degradations by using MW irradiations. For example, PET solvolysis occurred in the short reaction times in comparison with conventional heating methods [30].

In the continuation of our experiments in PU glycolysis [31-34], we decided to investigate the glycolysis of flexible PU foam using glycerin as decomposing agent under microwave irradiation at atmospheric pressure.

Experimental

Materials and instruments

Flexible cold cure PU foam, prepared by Daltoflex® EC 20240 (formulated virgin polyol containing propylene oxide–ethylene oxide copolyether, aliphatic amine catalysts, surfactant and water) and MDI, was used in recycling process. The polyol was a colorless viscous liquid and its characteristics were viscosity 1.250 Pa.s at 20 °C; specific gravity 1.035 g.cm^{-3} at 20 °C; fire point 240 °C; Mw ~ 1900; functionality 2 and hydroxyl number 59 mg KOH.g^{-1}. The isocyanate was Suprasec® 2027, diphenylmethane diisocyanate (MDI) based prepolymer. The MDI was a dark brown liquid with viscosity 0.220 Pa.s at 25 °C; specific gravity 1.23 g.cm^{-3} at 25 °C; NCO value 30.9 % by wt NCO groups analysis (group weight : 42 g.mol^{-1}); average functionality 2.7; flash point 233 °C and fire point 245 °C. Daltoflex EC 20240 and Suprasec 2027 are chlorofluorocarbon (CFC) free systems, purchased from HUNTSMAN® with starting formulation as (Daltoflex EC 20240: 100 *pbw*, Suprasec 2027: 65 *pbw*, recommended mold temperature: 40-45 °C; demolding time 5 min.; molding density: 42-47 kg.m^{-3}).

The experiments were performed in a Milestone MicroSYNTH "NP" Ethos 1600 microwave oven. FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopic techniques were utilized for characterization of recycled products and comparisons with virgin one. FT-IR spectra were recorded by a BRUKER Tensor 27 spectrometer (droplet samples were impregnated on KBr pellets). ^{1}HNMR and ^{13}CNMR spectra were recorded by a BRUKER CRX 300 instrument while acetone-d$_6$ was the solvent.

Typical glycolysis reaction

Glycerin (10 g) and catalyst (0.1 g) were placed in reaction vessel and irradiated in the microwave oven until obtaining a homogenous solution. After cooling at room temperature, grinded waste PU foam (5-10 mm particle diameter, 10 g) was added into the reaction mixture, being exposed to irradiation. In order to investigate the effect of reaction temprature, the glycolysis process was performed at 160, 180, 200 and 220°C in MW irradiation programs detailed in table 1.

Table 1. Applied MW irradiation program in glycolysis process at different reaction temperatures.

Fixed Temperature	Step	Time	Temperature	Maximum Power
160ºC	1	2 minutes	Ramp to 160ºC	Up to 700 Watt
	2	2 minutes	Hold at 160ºC	Up to 400 Watt
180ºC	1	1.5 minutes	Ramp to 180ºC	Up to 800 Watt
	2	2 minutes	Hold at 180ºC	Up to 800 Watt
200ºC	1	1.5 minutes	Ramp to 200ºC	Up to 900 Watt
	2	2 minutes	Hold at 200ºC	Up to 500 Watt
220ºC	1	1.5 minutes	Ramp to 220ºC	Up to 1000 Watt
	2	2 minutes	Hold at 220ºC	Up to 600 Watt

In all reactions the complete disappearance of foam particles was aimed as final dissolution time. In some reactions, 10-30 seconds additional time after perfect foam dissolution was needed to achieve the complete breakdown of urethane linkages.

At the end of reaction, mixture was removed from microwave oven, being filtered in order to isolate solid contaminants and un-reacted foam. Filtered liquid was allowed to split into two phases. The upper phase was the recovered polyol and the lower phase consisted of transesterification by-products and un-reacted glycerin. After centrifuging of the upper phase, its specifications was characterized and compared with virgin polyol.
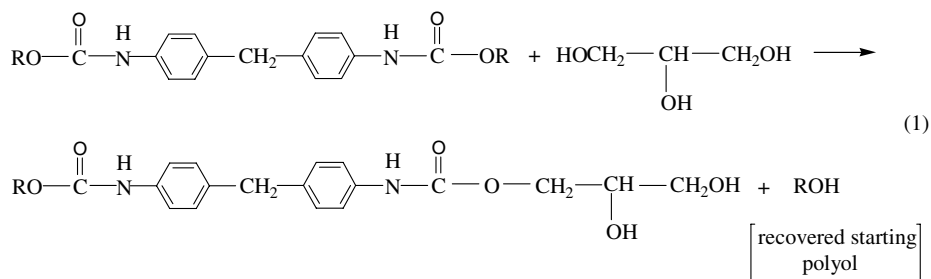
Results and discussion

In order to study the effect of microwave irradiations on glycolysis reactions, various reaction times, different temperatures and catalysts were examined. In this research, glycerin together with KOH or NaOH (100:1 weight ratio) was selected as destroying agent. In order to find the best dissolution time, all reactions were repeated for 3 times. The obtained average reaction times have been listed in table 2.
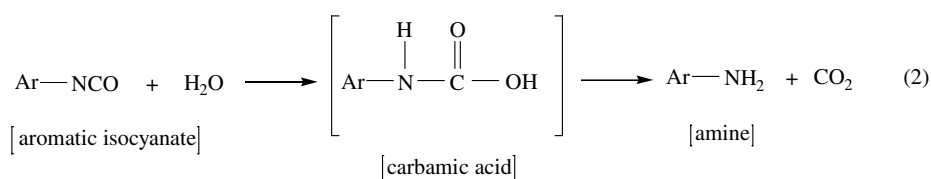
Table 2. Foam dissolution times at various temperatures using different catalysts.

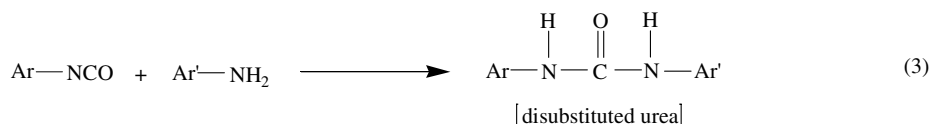| Temperature (ºC)	Time (s)	
	KOH	NaOH
160	110	93
180	92	81
200	78	79
220	67	65

The transesterification reaction was performed by glycerin/NaOH or KOH system leading to chain fracture of polyurethane linkage according to the equation 1:

$$RO-\underset{O}{\overset{O}{C}}-\underset{H}{N}-\bigcirc-CH_2-\bigcirc-\underset{H}{N}-\overset{O}{C}-OR \ + \ HOCH_2-\underset{OH}{CH}-CH_2OH \longrightarrow$$

$$(1)$$

$$RO-\overset{O}{C}-\underset{H}{N}-\bigcirc-CH_2-\bigcirc-\underset{H}{N}-\overset{O}{C}-O-CH_2-\underset{OH}{CH}-CH_2OH \ + \ ROH$$

$$\left[\begin{array}{c}\text{recovered starting}\\ \text{polyol}\end{array}\right]$$

The reaction mixture was separated into two phases. Lower phase contains wide variety of by-products obtained from transesterification reaction of urea, urethane and allophanate functional groups as well as decarboxylation by-products. In other words, used water-as a foaming agent-in polyurethane foam production, reacts with NCO group and forms unstable intermediate carbamic acid, which results in elimination of CO_2 and formation of primary amine group. The formed amine group reacts with NCO functional group to form urea bonds (equations 2 and 3) [35]:

$$Ar-NCO \ + \ H_2O \longrightarrow \left[Ar-\underset{H}{N}-\overset{O}{C}-OH\right] \longrightarrow Ar-NH_2 \ + \ CO_2 \quad (2)$$

$$\left[\text{aromatic isocyanate}\right] \qquad \left[\text{carbamic acid}\right] \qquad \left[\text{amine}\right]$$

The primary amine group reacts immediately with additional isocyanate group and fallowed by urea bond formation:

$$Ar-NCO \ + \ Ar'-NH_2 \longrightarrow Ar-\underset{H}{N}-\overset{O}{C}-\underset{H}{N}-Ar' \quad (3)$$

$$\left[\text{disubstituted urea}\right]$$

The upper phase containing recovered polyol was characterized by spectroscopic methods.

Figure 1 shows the FT-IR spectrum of Daltoflex EC 20240 virgin polyol.
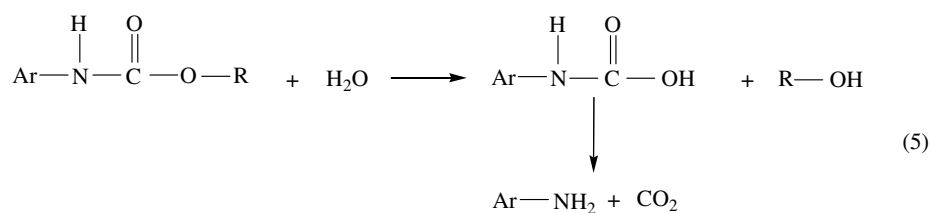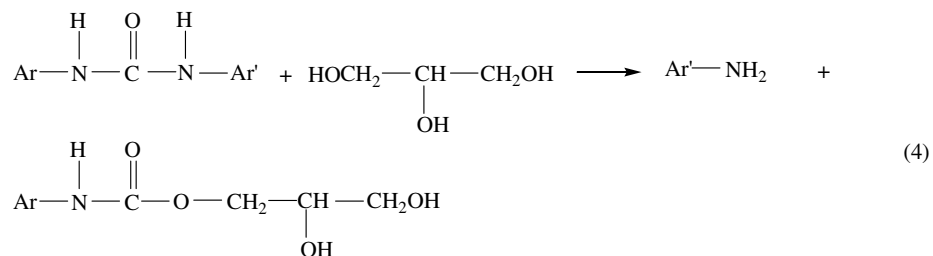
As shown in figure 1, absorption band at 1115 cm^{-1} is due to stretching vibrations of the aliphatic ether groups together with the signal produced by CO groups associated to hydroxyl end groups as overlapping and the stretching vibrations of these OH groups are at 3482 cm^{-1}. The absorption bands in 3000-2868 cm^{-1} spectral region are corresponding to stretching vibrations of CH bonds and bands at 1456 and 1374 cm^{-1} characteristic are corresponding to bending vibrations of methylene and methyl groups in the polyol chain [14]. The FT-IR spectra of recovered polyols in various reaction temperatures and in presence of KOH or NaOH catalysts were similar to the virgin one (Figures 2, 3 respectively).

As can be observed in figures 2 and 3, only a few slight differences are found between FT-IR spectra of virgin and recovered polyols. Probably the absorption bands at >3000 cm^{-1} in recovered polyols' spectra would be broader, due to the presence of
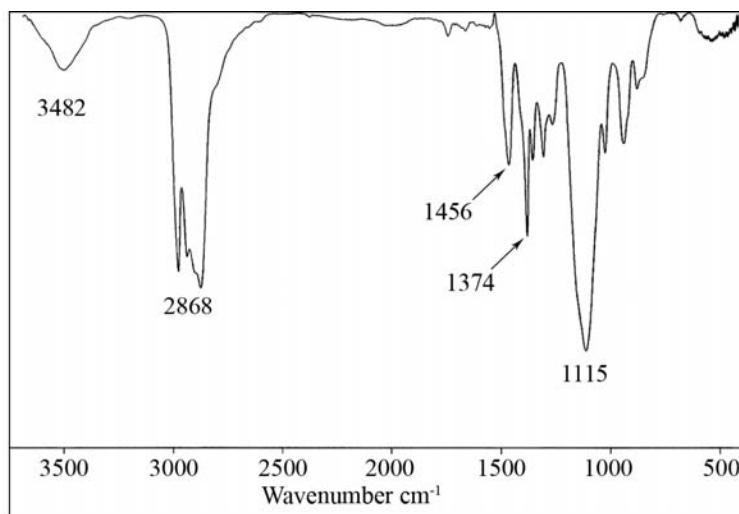
**Figure 1.** FT-IR spectrum of Daltoflex EC 20240 polyol.

NH_2 functional groups of primary amines in the upper phase as contaminant. 4, 4´-methylenediphenyl diamine is one of the reaction by-products which obtain during glycolysis reaction due to transesterification of urea groups existing in the urethane chains or hydrolysis reaction. The trapped water molecules in PU wastes are responsible for this reaction [1]:

$$\underset{\underset{\displaystyle H}{|}}{Ar-N}-\underset{\underset{\displaystyle}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-Ar' \;+\; HOCH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2OH \longrightarrow Ar'-NH_2 \;+\;$$

$$\text{(4)}$$

$$Ar-\underset{\underset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle}{\|}}{C}-O-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2OH$$

$$Ar-\underset{\underset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle}{\|}}{C}-O-R \;+\; H_2O \longrightarrow Ar-\underset{\underset{\displaystyle}{|}}{N}-\underset{\underset{\displaystyle}{\|}}{C}-OH \;+\; R-OH$$

$$\text{(5)}$$

$$Ar-NH_2 \;+\; CO_2$$

Therefore new absorption bands at 1617 and 1516 cm^{-1} are related to the bending vibrations of amine groups derived from 4, 4´- methylenediphenyl diamine which slightly has been dissolved in the upper phase. Although small portion of glycerin is dissolved in the upper phase, no observable changes in absorption bands are appeared except signal widening in > 3000 cm^{-1} spectral region. Because all stretching vibrations of glycerin bonds (C-O and OH bonds) locate in the same spectral regions of C-O and OH bonds of virgin polyol.
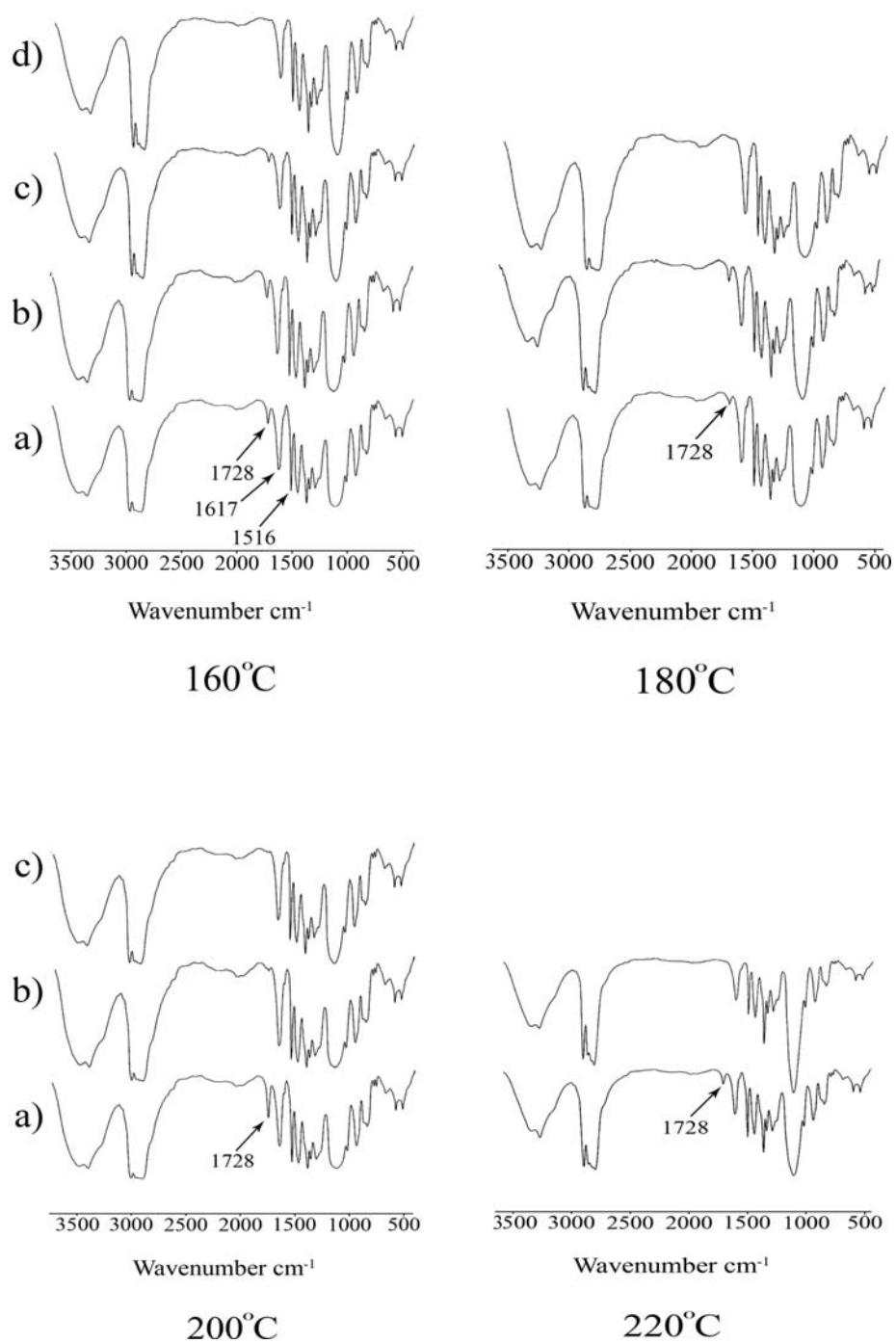
Figure 2. FT-IR spectra of the recovered polyols at different temperatures in the presence of KOH as catalyst. Extended reaction times for glycolysis reaction completion are: a) 0, b) 10, c) 20 and d) 30 seconds after perfect foam dissolution.
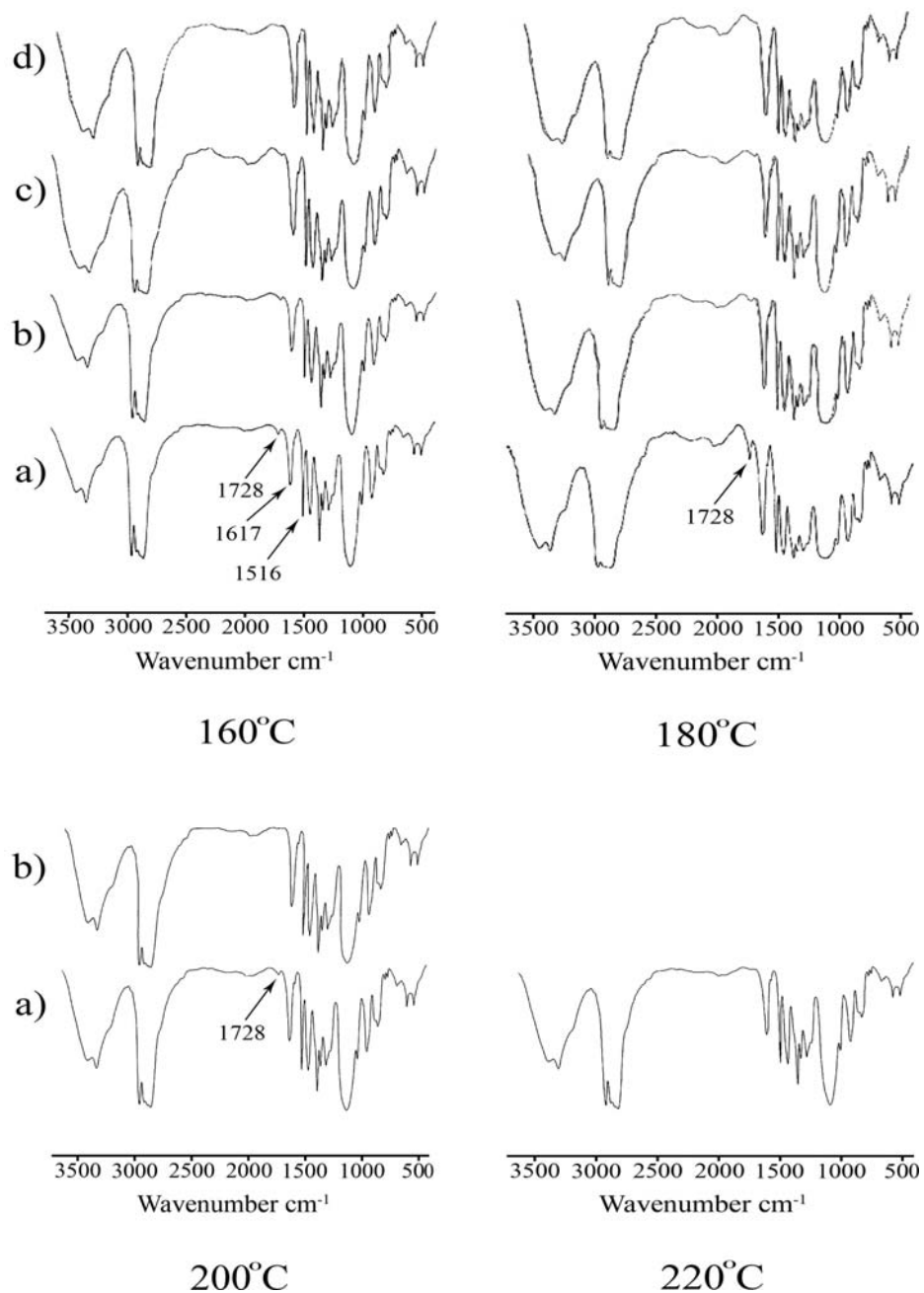
Figure 3. FT-IR spectra of the recovered polyols at different temperatures in the presence of NaOH as catalyst. Extended reaction times for complete glycolysis reaction are: a) 0, b) 10, c) 20 and d) 30 seconds after perfect foam dissolution.

Bands assigned to the stretching vibrations of the carbonyl groups in urethane linkage are found in the 1749-1690 cm^{-1} [14]. Therefore the stretching vibrations in the spectral region 1728 cm^{-1} in figures 2 and 3 is corresponding to urethane groups, which their intensity is decreased by increasing reaction time. The glycolysis reaction was completed with disappearance of the stretching vibration of urethane group at 1728 cm^{-1}. One of the most important observations in these reactions was the dependence of urethane band disappearance times to the catalyst type and the reaction temperature. These results are concluded from figures 2 and 3. In figure 2, in the presence of KOH, the reaction time decreased from 30 to 10 s when temperature was risen from 160 to 220°C. While the utilization of NaOH catalyst in the higher temperature (220°C) represented the perfect destroying of polymer chains immediately after perfect foams dissolution (Figure 3).

Figure 4 shows FT-IR spectra of the lower phase sampled at different reaction times. Similar to the upper phase, the presence of absorption bands at 1614 and 1515 cm^{-1} as well as two weak signals at 512 and 572 cm^{-1} confirm formation of amine compounds which concentrated in the reaction mixture with passing of time [36].
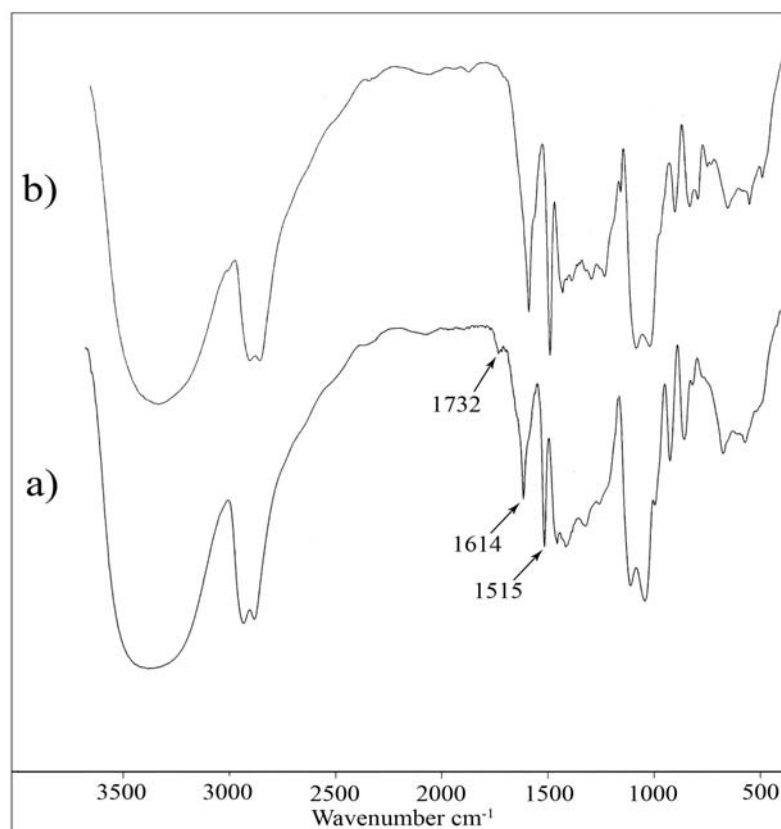
Figure 4. Comparison of FT-IR spectra of obtained products in the lower phase in presence of NaOH at 160°C and at different reaction times: a) 0 and b) 30s after perfect foam dissolution.

NMR spectroscopy method was utilized for investigation the chemical structure of recovered polyol and comparison with virgin one. Figure 5 shows ^{1}HNMR and ^{13}CNMR spectra of virgin polyol [37,38].
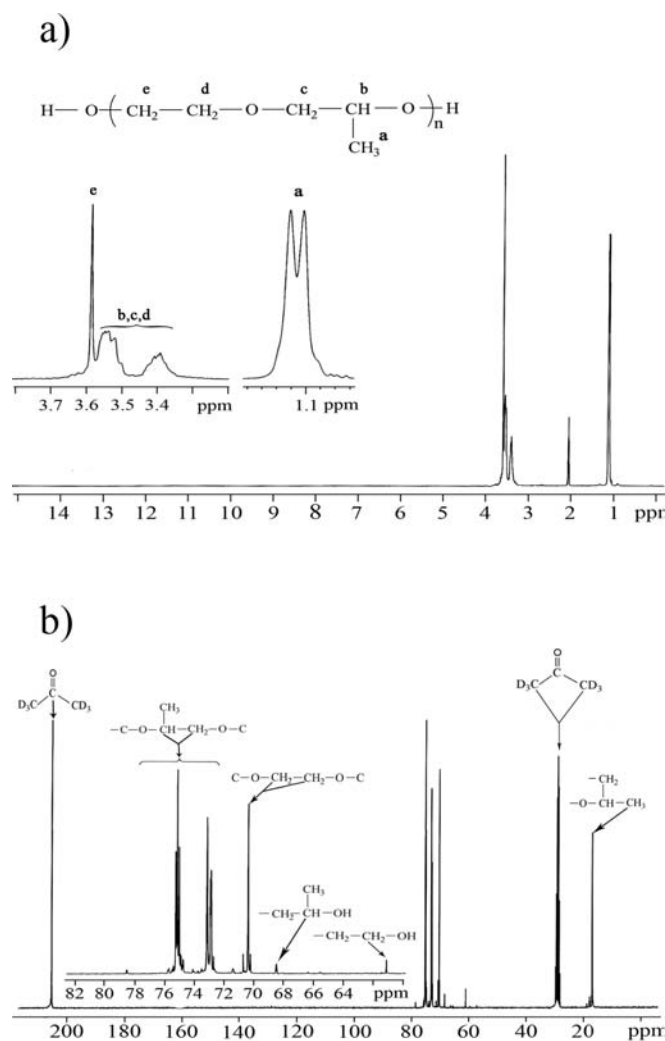

Figure 5. ^{1}HNMR (a) and ^{13}CNMR (b) spectra of virgin polyol.

In ^{1}HNMR spectrum, the peak at 1.1 ppm is corresponding to methyl hydrogen's and the peaks at 3.0-4.0 ppm are relative to hydrogen's directly connected to C-O groups [39]. The quintet peak in 2.05 ppm is corresponding to deuterated acetone. ^{1}HNMR and ^{13}CNMR spectra of the recovered polyols at lowest and highest reaction temperatures (160 and 220°C) at the end point of reaction namely after complete breakdown of urethane linkages have been shown in Figures 6 and 9 respectively.
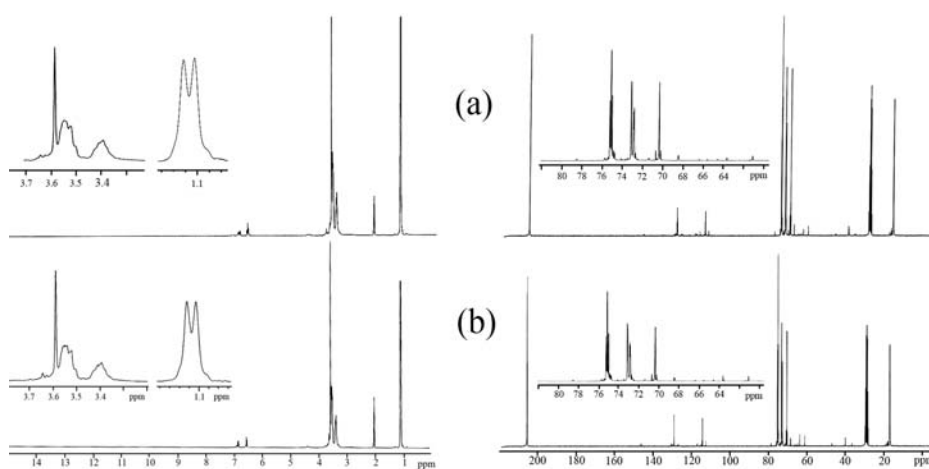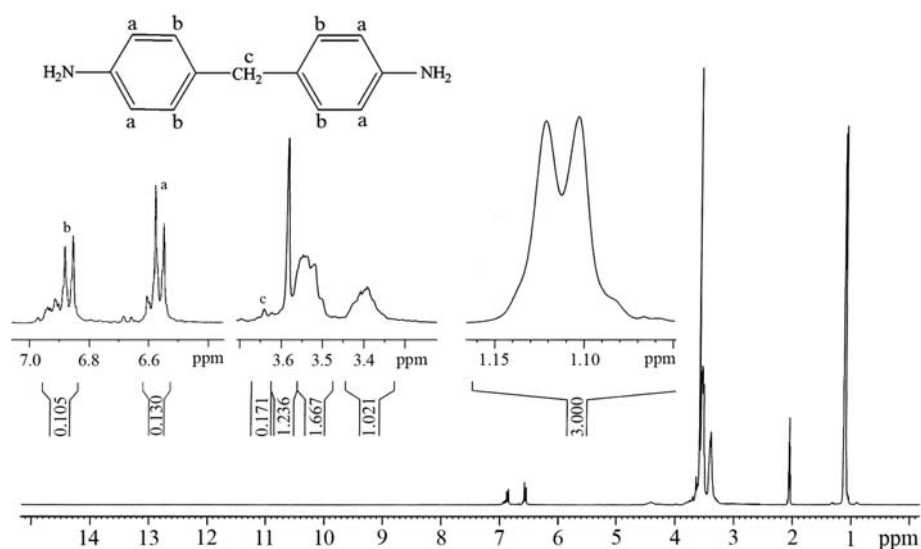
Figure 6. ¹HNMR and ¹³CNMR spectra of recovered polyol at complete reaction time (30 s) in presence of, (a) NaOH and (b) KOH at 160°C.

δ in ppm	Carbon
40	e
114.5	b
130.5	d
129	c
146	a
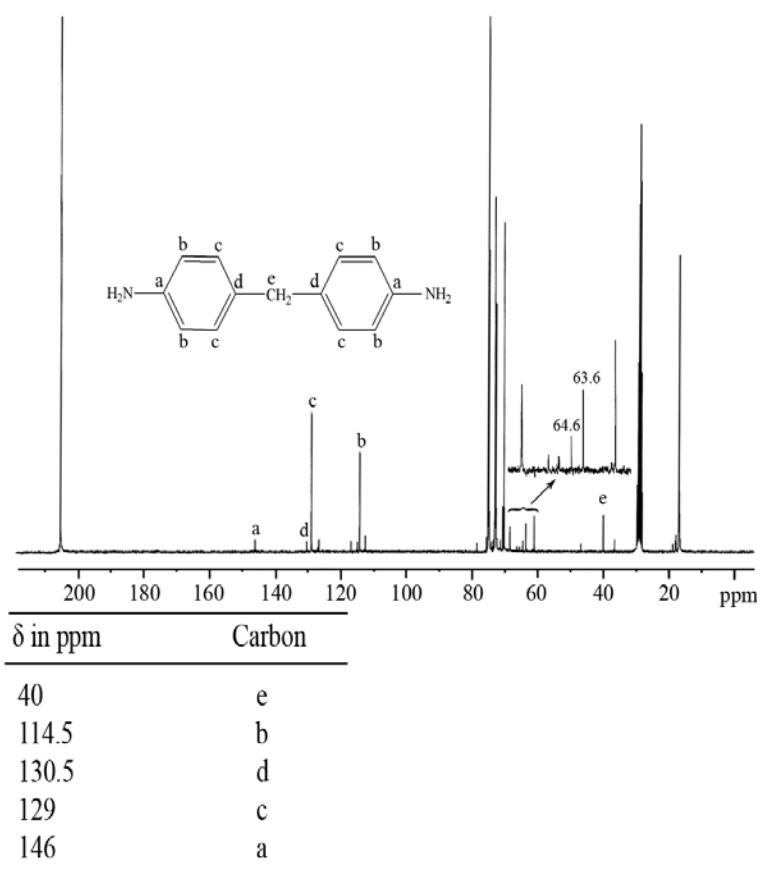
Figure 7. The spectral regions associated to the transesterification by-products remained in the upper phase indicated in ¹³CNMR spectrum of recovered polyol.

In figure 6 the similarity of chemical structure of recovered polyol to the virgin one is clear. But there are several additional peaks in ^{1}HNMR and ^{13}CNMR spectra of recovered polyols in comparison with virgin one. In ^{13}CNMR spectra, the signals at 110-150 ppm are associated to carbons derived from the starting isocyanate. The additional peaks at 40, 114.5, 130.5, 129 and 146 ppm in ^{13}CNMR spectrum of recovered polyol (figure 7) are caused by aromatic diamine compounds [40]. Also the weak signals at 63.6 and 64.6 ppm are the typical bands of carbons bearing hydroxyl end groups associated to the transesterification by-products formed by the substitution of polyol by glycerin molecules. In addition, no absorption band is observed at 156 and 164 ppm to indicate the presence of the urethane and urea carbonyl bonds respectively [41] thus the complete recovery of polyol in microwave irradiation condition is confirmed.

Figure 8 shows the peaks observed at 3.64, 6.5-6.6 and 6.8-6.9 ppm in ^{1}HNMR spectrum of recovered polyol which correspond to the aromatic diamine compounds remained in the upper phase as well as hydrogen peak areas. The integration of contaminants and recovered polyol corresponding hydrogen peak areas showed the polyol contamination as 4.0%.

Figure 8. The ^{1}HNMR spectral regions associated to the transesterification by-products (aromatic diamine compounds) remained as contaminant in the upper phase.

Figure 9 shows the ^{1}HNMR and ^{13}CNMR spectra of recovered polyol at 220°C. All the spectral regions are quite similar to figure 6.

Application of microwave irradiation accelerates the glycolysis reactions in comparison with conventional methods. In order to prove this claim, we examined a typical reaction at 180°C with conventional heating method and required time for perfect foam dissolution measured and compared to microwave technique. All conditions such as geometry and foam particle size, solvent, catalyst and its concentration as well as solvent/foam ratio in both methods were quite similar together. The obtained results represented the ability of MW in reduction of reaction time from 29 minutes to
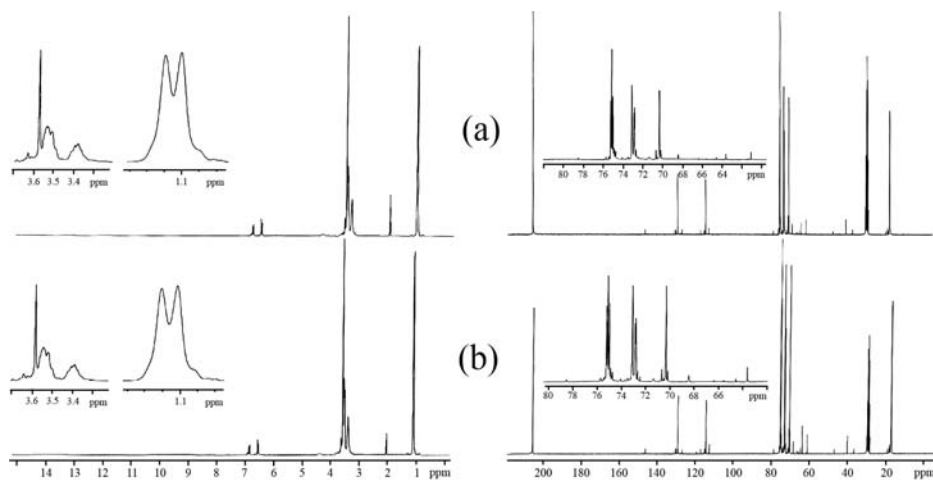
Figure 9. ^{1}HNMR and ^{13}CNMR spectra of recovered polyol at 220°C, (a) in presence of NaOH after immediately perfect foams dissolution and (b) at 10 s reaction time in presence of KOH.

92 seconds in KOH accelerated reaction and from 42 minutes to 81 seconds in NaOH catalyzed process (Figures 10 and 11 respectively).
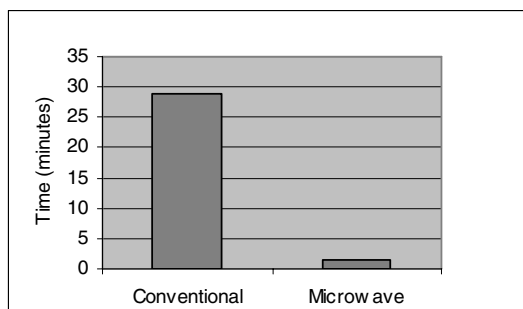
Figure 10. Comparison of complete foam dissolution times in the presence of KOH at 180°C in microwave and conventional heating conditions.
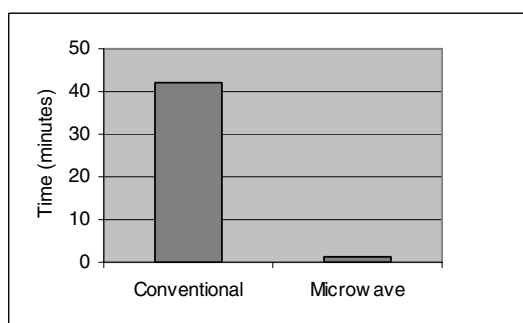
Figure 11. Comparison of complete foam dissolution times in the presence of NaOH at 180°C in microwave and conventional heating conditions.

Conclusions

The glycolysis reaction of cold cure flexible PU foams was performed in a Milestone MicroSYNTH "NP" Ethos 1600 microwave oven at atmospheric pressure. In order to obtaining high quality recovered polyols via "split-phase" condition and short reaction times, glycerin and sodium or potassium hydroxides were used as solvent and catalysts, respectively. Reactions were carried out at various temperatures namely 160, 180, 200 and 220°C. Decreasing of reaction time was observed by the increasing in reaction temperature. On the order hand, microwave irradiation accelerated the conversion reaction 20-30 times faster than conventional heating methods. The FT-IR spectra of recycled polyols at different conditions were quite similar to virgin one, except 3 new absorption bands at 1617 and 1516 cm^{-1} corresponding to the bending vibrations of amine N-H bonds that slightly had been dissolved in the upper phase and at 1728 cm^{-1} due to the urethane absorption band that its intensity decreased with increasing reaction time. According to these results, microwave can be used as an energy source in glycolysis reactions and their performance at short time with simple controlled conditions.

References

1. Scheirs J (1998) Polymer recycling: science, technology and applications. John Wiley & Sons Ltd, England
2. Grigat E (1978) Kunststoffe 68(5):281
3. Mahoney LR (1980) Hydrolysis of polyurethane foams. US Patent 4,196,148
4. Johnson OB (1977) Method for continuous hydrolysis polyurethane foam in restricted tubular reaction zone and recovery. US Patent 4,025,559
5. Pat Fr (1966) 1429011, CA (1966) 65 9124e
6. Pat Fr (1968) 1484107, CA (1968) 68 13679g
7. Simioni F, Modesti M, Rienzi SA (1987) Cell Polym 6:2741
8. Bauer G (1991) Recycling of polyurethane wastes and mixed polymer wastes by means of alcoholysis reaction. In: Polyurethanes World Congress 1991. The Society of the Plastic Industry, Inc. and The European Isocyanate Producers Association, New York
9. Simioni F, Bisello S, Tavan M (1983) Cell Polym 2:281
10. Fedenyuk PV, Baramboin NK (1987) Izv Vyssh Uchebn Zaved Teknol Legk Prom Moscow 30(4):51
11. Kanaya K, Takahashi S (1994) J Appl Polym Sci 51:675
12. Modesti M, Simioni F, Munari R, Baldoin N (1995) React Funct Polym 26:157
13. Chao-Hsiung WU, Ching-Youan C, Chien-Min C, Hung-Chang H (2003) Polym Degrad Stab 80:103
14. Molero C, Lucas A, Rodriguez JF (2006) Polym Degrad Stab 91:221
15. Ulyanov VP, Morozov YUL, Al'tev Yu M, Gudimenko VI, Tkachuk AP, Sharapov RI (1987) Kozu- Obuvn Prom-st 10:20
16. Gedye R, Smith F, Westaway K, Ali H, Baldisera L, Laberge L, Rousell J (1986) Tetrahedron Lett 27:279
17. Giguere RJ, Bray TL, Duncan SM (1986) Tetrahedron Lett 27:4945
18. Ludlow-Palafox C, Chase HA (2001) Ind Eng Chem Res 40:4749
19. Jacob J, Chia LHL, Boey FYC (1996) J Appl Polym Sci 63:787
20. Correa R, Gonzalez G, Dougar V (1998) Polym 39:1471
21. Albi T, Lanzon A, Guinda A, Leon M, Perez-Camino MC (1997) J Agri Food Chem 45:3795
22. Caddick S (1995) Tetrahedron 51:10403
23. Lidström P, Tierney J, Wathey B, Westman J (2001) Tetrahedron 57:9225

24. Kappe CO (2004) Angew Chem Int Ed 43:6250
25. de la Hoz A, Díaz-Ortiz A, Moreno A (2004) Curr Org Chem 8:903
26. Kuhnert N (2002) Angew Chem Int Ed 41:1863
27. Strauss CR (2002) Angew Chem Int Ed 41:3589
28. Gedye RN, Wei JB (1998) Can J Chem 76:525
29. Perreux L, Loupy A (2001) Tetrahedron 57:9199
30. Krzan A (1998) J Appl Polym Sci 69:1115
31. Alavi Nikje MM, Nikrah M (2007) Polym Bull 58:411
32. Alavi Nikje MM, Nikrah M (2007) Polym Plast Techol Engin (in press)
33. Alavi Nikje MM, Haghshenas M, Bagheri Garmarudi A (2006) Polym Bull 56(2-3):257
34. Alavi Nikje MM, Haghshenas M, Bagheri Garmarudi A (2006) Polym Plast Technol Engin 45(4):569
35. Szycher M (1999) Handbook of Polyurethanes. CRC Press LLC, Florida
36. William W. Simons (1978) the Sadtler Handbook of Infrared Spectra. Sadtler Research Laboratories, Inc., United States of America, p. 165
37. Standard Test Methods for Polyurethane Raw Materials Determination of Primary Hydroxyl Content of Polyether Polyols. D 4273-05 Book of Standards Volume: 08.02
38. Lebas CL, Turley PA (1985) J cell Plast 20(33):194
39. Pegoraro M, Galbiati A, Ricca G (2003) J Appl Polym Sci 87:347
40. http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi
41. Kanaya K, Takahashi S (1994) J Appl Polym Sci 51:675