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# Application of Factorial Design Method for the Optimization of Reaction Conditions Influencing Viscosity of Poly(amide-imide-ether-urethane)s Based PEG and L-Leucine

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# ABSTRACT

or the first time, we report the optimization of reaction conditions for the synthesis of novel thermally modified optically active poly(amide-imide-ether-urethane)s (PAIEU)s prepared by diisocyanate route. The effects and importance of different reaction parameters such as reaction temperature, reaction time, and soft segment length on the controlling of chain growth of the resulting copolymers were investigated. Thus, four different series of PAIEUs based on different molecular weight of polyethylene glycol (PEG)s were synthesized through the reaction of a new imide containing diacid, with 4,4'-methylene-bis-(4-phenylisocyanate) (MDI). A linear correlation was constructed using experimental values of viscosities of the resulting copolymers based different molecular weights of PEGs at different reaction temperatures, and reaction time. The influence of each parameter was studied by factorial design analysis. Analysis of variance (ANOVA) was also used to evaluate the significance of the linear regression model (correlation). The statistical parameters reveal strong evidence that the constructed correlation is reliable.

## **Key Words:**

mathematical optimization; experimental design; poly(amide-imide-ether-urethane); computer modelling; polyurethanes.

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# INTRODUCTION

It is common that, in order to study the effect of certain variables (a factor or stimulus) on some systems, several subjects are observed in the presence of the variable and identical subjects are observed in the absence of the same variable with all other factors held constant. This is a very popular design in research, industry, and quality control, especially used by an analchemist [1-4]. Another approach is randomized design in which, subjects are randomly assigned to the various treatments with the assumption that, all subjects are

observed under identical conditions except for the factor(s) being tested however, this is not generally true. In m×m Latin square design method, each entry is expressed as x<sub>iik</sub> where i stands for the number of rows, j for the number of columns, and k for the number of treatments. The variation in the Latin square entries is the sum of the variations between rows (dayto-day), the variations between columns (tester-totester), the variations between treatments (sample-tosample), and the basic assumption is that these components act independently. While, in practice they may interact to some degree [1]. There are numerous cases where the under-laying factors do not display their effects independently. Since the effect of each factor is certain to depend on the level of the others, the experiment is bound to yield a fake image of the effect of each factor and, is incapable of detecting the effect of the inter-dependence of both (or other) factors. Thus, phenomena that involve factors whose effects are not independent of the levels of other factors must be examined by varying all factors simultaneously. Conducted in this manner, the experiment yields the effect of each factor accurately and evaluates the effects of the interactions between them [1]. The technique called one variable at a time or OVAT, used in conventional experimentation techniques cannot quantitatively explore the influence of combined factor effects on the response. This experimental design method cannot only serve as an aid to have a clearer image about the effect of all variables on the properties but enable to locate the region where the properties are optimized [5]. Factorial design is one of the most popular class of experimental designs that are often used to investigate multifactor response surfaces. In the other words, factorial design analysis is a statistical study in which each observation is categorized according to more than one factor. Such an experiment allows studying the effect of each factor on the responsible variable, while requiring fewer observations than conducting separate experiments for each factor independently. It also allows studying the effect of the interaction between factors on the response variable [6].

ANOVA helps the researchers to decide which factors display significant effects on the results, but it does not give any information about how the factors affect the results. It is sufficient for most experiments involving only qualitative factors (e.g., type of catalyst or polyol). For quantitative factors (e.g., temperature or concentration) it can be understood how much a factor affects the results, by evaluating a quantitative relationship between the factors and the results. Thus, correlation of experimental data is an essential tool for research and analysis endeavors. It aids in establishing the quantitative relationships between results and experimental variables and conditions. Also correlations can be used to optimize experimental conditions [1] as well as understanding relationships between material properties and its micro-structures, many physical phenomena and preparation conditions. This understanding gives a technological basis for controlling material properties and creating new materials [7]. As computer is becoming a useful tool in many areas of engineering (such as architectural, mechanical and electrical engineering), there is a growing expectation for simulation tools for material engineering [7-10]. However, although it has found some successes in some areas, the technology is still at a primitive stage. The major reason for this is that material properties depend on many factors which cannot be handled by a single simulator [7].

A number of journals are dedicated to mathematics that can be used to control systems of all descriptions and their application to problems such as optimization of industrial production processes. Chemists use control and optimization methods either directly or indirectly. For example, organic or polymer chemist is making an attempt at system optimization when the parameters of a new synthetic reaction are changed in a challenge to optimize product yield, viscosity, thermal or mechanical properties [1]. The combination of a laboratory approach with statistical analysis provides a correlation, which can be used to investigate correlations with material properties [11,12].

Polyurethanes (PUs) are versatile polymers and can be easily formed by a simple polyaddition reaction of polyol, diisocyanate and a chain extender. The tailor-made properties of PUs from super soft flexible foams to tough elastomers and to long-wearing coatings have resulted in many final applications [13,14]. The widely known importance of PUs in many industrial fields has resulted in an increase in many research works on this subject [9-17] and there are numerous studies on the influence of chemical composition and structure property relationships [18,19]. Because, there are many parameters that influence PUs chain growth, properties and processing, it has been found that the properties of the final PUs can be controlled and adjusted to any specific application by optimizing the reaction condition, pre-polymerization and chain extension steps [2-4,8,20-22].

In addition, synthesis of optically active polymers is a topic that has been paid more attention. Specially, the synthesis of polymers containing amino acids is a subject of much interest, since a high degree of amino acid functionality can lead to polymers with increased solubility and the ability to form secondary structures [23,24]. Possible applications of amino acid-based polymers include drug delivery agents, chiral recognition stationary phases, asymmetric catalysts, metal ion absorbents, and biomaterials [25,26].

In connection with our interest in preparing thermally modified optically active PUs, by introducing the imide and amide functions in their backbone [27-32], according to experiments we thought that many parameters such as reaction temperature, reaction time, reaction catalysts, reaction solvent, soft segment length and type, method of preparation, addition of chain extender and so on, influence the properties of copolymers including solubility, viscosity, thermal behaviour, etc. Thus, in this work we set out to investigate the effect of different reaction conditions on the polymer chain growth to determine the optimized condition by establishing a linear correlation between the viscosities of the resulting polymers and different experimental conditions.

## EXPERIMENTAL

Specific rotations were measured by a Jasco Polarimeter to confirm the incorporation of bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine (BPABTL) (1) [33] with amino acid moiety in PU backbone. The data were processed with a written algorithm with MATLAB (the Math Work Inc., Version 4) by the authors.

### Synthesis of Segmented PAIEU Copolymers

A typical preparation of PAIEUs according to (diacid: MDI: polyol) molar ratio of (1:2:1) was as follows:

Into a dried 10 mL round-bottom flask BPABTL (1)  $(0.0569~g,\ 1.04{\times}10^{-4}~mol)$  and MDI (0.0524~g, $2.09 \times 10^{-4}$  mol) in 0.23 mL of NMP were dissolved. The reaction was stirred at room temperature (RT) for 2 h; between 50-60°C for 2 h; 60-80°C for 2 h; at 80°C for 5 h; 80-120°C for 2 h; and finally at 120°C for 2 h. To this solution PEG-1000 (0.1046 g, 1.046×10<sup>-4</sup> mol) in 0.25 mL of NMP was added at RT. Then the reaction was stirred at RT for 1 h; between 50-60°C for 2 h; 60-80°C for 2 h; at 80°C for 5 h; 80-120°C for 2 h and finally at 120°C for 1 h. The viscous solution was poured into 10 mL of water, to isolate the polymer. The precipitated polymer was collected by filtration, and was dried at 80°C for 6 h under vacuum to give 0.19 g (93 %) of polymer. The reaction conditions for experimental design method for step 2 were selected according to Table 1.

The above polymerizations were repeated by using PEG-400, PEG-600, and PEG-2000 under different reaction conditions such as reaction catalysts, reaction temperature, reaction time, and reaction solvent.

#### **RESULTS AND DISCUSSION**

#### **Polymer Synthesis**

Four series of PAIEUs based on different molecular weights of PEG soft segments, were synthesized (Scheme I). First, OVAT technique was used to study the effects of different reaction conditions such as reaction catalysts (TEA, Py, dibutyltin dilurate (DBTDL) and without catalyst), reaction solvent (NMP, DMF, DMAc), solvent to solid ratio, while PEG-400 was used as soft segment [27,28,30]. The optimized condition was set according to our previous work, thus the polymerization reactions were performed with the molar ratio of diacid:MDI:PEG of (1:2:1), in NMP as optimized solvent with the ratio of solvent to solid of 2-2.5 (V/W) in the absence of any catalyst. Then, viscosities of the final PAIEUs were considered as a function of reaction temperature and reaction time of step 2, as well as soft segment length (PEG-400, 600, 1000, and 2000) (Scheme I). The coefficients of these parameters were obtained by multiple linear regression method. First, a preliminary study showed that the viscosity of final PAIEUs was more sensitive to reaction temperature and time

23

Soft segment	Temperature	Reaction	Inherent viscosity	$[\alpha]^{25}$
molecular weight	(0)	une (n)	(uL/g)	$[\alpha]_D$
400	100	6.33	0.207	-2.3
400	70	5.00	0.262	+2.5
400	60	5.50	0.273	+3.1
400	140	8.00	0.291	+3.0
400	50	4.42	0.314	+3.7
400	80	3.00	0.329	+4.0
400	140	1.50	0.404	+3.9
600	140	7.00	0.114	-2.4
600	100	4.50	0.163	-1.1
600	50	1.03	0.247	+2.3
600	65	6.17	0.336	+3.5
600	50	5.00	0.419	+4.5
600	85	2.00	0.722	+4.1
600	140	1.20	0.482	+4.5
1000	140	4.00	0.104	-2.7
1000	55	4.10	0.174	-2.5
1000	90	6.25	0.212	+2.6
1000	100	4.25	0.254	+2.7
1000	50	4.50	0.308	+3.0
1000	70	2.00	0.339	+3.4
1000	140	1.50	0.464	+4.2
2000	90	4.08	0.240	-1.7
2000	50	4.50	0.275	-2.0
2000	75	5.00	0.290	+2.7
2000	60	6.00	0.302	+3.0
2000	50	1.25	0.337	+4.6
2000	140	1.50	0.427	-3.1

 Table 1. Laboratory conditions (Step 2) of 27 experiments that designed to construct the correlation.



PEG

Scheme I. Preparation of a NCO-terminated oligo amide-imide (Step 1) and chain extension by PEG polyether polyol (Step 2).

during step 2, thus the effect of these parameters on the polymer chain growth or depolymerization was studied by factorial design method. It means that reaction temperature and time length during step 2 were selected randomly according to factorial design method. The reaction stages for reaction temperature and time during step 1 of polymerization reactions were set as: stirring at RT for 2 h; between 50-60°C for 2 h; 60-80°C for 2 h; at 80°C for 5-6 h; 80-120°C for 2 h; and finally at 120°C for 2 h. For each factor, the parameter coefficient, the standard error, the t value for the null hypothesis (H<sub>0</sub>), and the corresponding P value were calculated. A program written in MATLAB was used to perform the calculations and constructing of the correlation.

#### **Model Study**

In order to determine the optimized condition for the preparation of a PAIEU with the highest viscosity; a linear correlation was constructed between the viscosities of the polymers and different experimental conditions applied on step 2. Thus, 27 experiments were designed, which their conditions are presented in Table 1. The variables of the experimental conditions for step 2 were considered as molecular weight of the PEG polyol (PEG-400, 600, 1000, and 2000), temperature (°C) and the reaction time (h). The temperature and reaction time for polymerization reactions during step 2 were ranged 50-140°C and 1-8 h, respectively. The data obtained from this study showed that at temperatures lower than 50°C; polymer chain growth cannot be well established and at temperatures higher than 140°C a drastic decrease of viscosity was observed because of depolymerization reaction and chain scissioning. Additionally, it can be seen that, all reaction time longer than 8 h resulted in no significant changes in the viscosities of the resulting polymers and only wastes energy and time. Therefore, 27 experiments were performed between the above mentioned temperatures ranges (50-140°C) and reaction time (1-8 h). According to data presented in Table 1, the highest viscosity which obtained was 0.7 (dL/g).

A linear correlation was constructed using experimental values of the viscosity of the resulting PAIEUs obtained under different reaction temperatures and time, and PEG molecular weights (eqn (1)).

$$\begin{split} &Y{=}-2.00\;(\pm0.34)-0.04\;(0.04)\;x_1+8.54\;(\pm1.12)\;x_2+\\ &3.90\;(\pm0.60)\;x_3-5.62\;(\pm0.77)\;x_2^2-15.13\;(\pm1.97)\;x_2\\ &x_3+2.15\;(\pm0.33)\;x_3^2x_2+8.48\;(\pm1.33)\;x_2^2x_3 \qquad (1) \end{split}$$

 Table 2. Calculated t values of the coefficients for the linear correlation.

Coefficient			Calculated t	
		Standard error	values	
constant	-2.00	±0.34	5.88	
x <sub>1</sub>	-0.04	±0.04	1.00	
x <sub>2</sub>	8.54	±1.12	7.62	
<b>X</b> 3	3.90	±0.60	6.5	
x <sub>2</sub> <sup>2</sup>	- 5.62	±0.77	7.30	
x <sub>2</sub> x <sub>3</sub>	-15.13	±1.97	7.68	
$x_3^2 x_2$	2.15	±0.33	6.52	
x <sub>2</sub> <sup>2</sup> x <sub>3</sub>	8.48	±1.33	6.37	

In this equation Y stands for the viscosity of the polymer,  $x_1$  molecular weight of the PEG soft segment,  $x_2$  temperature and  $x_3$  is the reaction time.

In order to evaluate the coefficients of the correlation, t-test was used to determine whether the considered parameters, or factors are significant or not. Calculated values of t which is equal to ratio of b/s (coefficient/standard error of the coefficient) are presented in Table 2. According to these data, it can be seen that all of the t values except for the t value corresponding to x1 (t = 1.00), are greater than the critical t value which is 1.71 (for degrees of freedom of 26 and 95% confidence interval). Thus, it means that this term (x<sub>1</sub>) should be eliminated from the equation and a new correlation without the molecular weight of the soft segment should be reconstructed. The new correlation is as follows:

$Y=-2.00 \ (\pm 0.35) + 8.52 \ (\pm 1.12) \ x_1 + 3.8$	36 (±0.61) x <sub>2</sub>
- 5.62 (±0.77) $x_1^2$ - 15.10 (±1.98) $x_1x_2$ +	2.19 (±0.33)
$x_2^2 x_1 + 8.46 (\pm 1.33) x_1^2 x_2$	(2)

In this equation Y is the viscosity of the polymer,  $x_1$  is the reaction temperature and  $x_2$  is the reaction time. It is worthy to mention that since there is not any term in this equation which represents the molecular weight of the soft segment; this variable is not an effective parameter on the viscosity of the copolymers. This conclusion can be confirmed by the data presented in Table 1. These data show that, there is no significant difference between the viscosities of polymers based on different molecular weight of PEGs

25



**Figure 1.** Experimental vs. calculated values of the viscosity for 27 experiments.

prepared under the same reaction temperature and time.

The curve of the experimental values for 27 experiments versus calculated values of the viscosities are shown in Figure 1. Theoretical values of the viscosities have been calculated from the linear correlation (eqn (2)).

ANOVA was also used to determine the significance of the linear regression model (correlation). The ANOVA data for the constructed linear correlation are given in Table 3. The F value is the ratio of

**Table 3.** The data related to the analysis of variance(ANOVA).

Sum of squares		df	Mean square	F	P value
Regression	0.407	6	0.068	22.70	0.000
Residual	0.055	20	0.003		
Total	0.462	26			



**Figure 2.** Three dimensional graph of theoretical viscosities of polymers that can be synthesized at different reaction temperatures and time.

 $MS_{Reg}/MS_{Res}$  (the mean square of the regression divided by the mean square of the residual). When the  $MS_{Reg}$  is much larger than the  $MS_{Res}$ , the ratio of  $MS_{Reg}/MS_{Res}$  is large and there is evidence against the null hypothesis. According to Table 3, the numerical value of F which is equal to 22.7 and the P-value for the F test which is less than 0.001, reveal strong evidence against the null hypothesis; which confirm the constructed correlation is reliable.

In order to evaluate the capability of correlation to predict the viscosity, four more experiments including different molecular weights of PEG, reaction temperature and time were randomly considered. Then the theoretical values of the viscosities were calculated using eqn (2). To compare experimental values of the viscosities of PAIEUs with predicted data calculated by eqn (2), four polymers were synthesized in the laboratory under the selected conditions by authors.

**Table 4.** The predicted and the experimental values of the viscosities for four different laboratory conditions.

Soft segment molecular weight	Temperature (°C)	Reaction time (h)	Experimental viscosity (dL/g)	Calculated viscosity (dL/g)	Absolute error
400	50	1.0	0.278	0.277	-0.001
600	95	2.5	0.531	0.555	-0.024
1000	50	0.75	0.262	0.286	0.024
2000	140	1.25	0.337	0.270	0.067

Table 4 shows these numerical values. Comparison of the predicted data calculated by eqn (2) and the experimental values of the viscosities show there is a good agreement between these data.

In the final step, different combinations of the reaction temperatures and time were selected and the viscosities were determined by correlation 2. Figure 2 shows three dimensional graphs of the viscosities of the polymers that can be synthesized at different reaction temperatures and time lengths. This study reveals that (Figure 2) PAIEU with the highest viscosity can be obtained at temperature of 85°C and the reaction time of 2 h, and PEG molecular weight does not play a significant rule.

### CONCLUSION

For the first time we successfully used mathematical method for the optimization of some of the reaction parameters, that can influence viscosity and polymer chain growth of thermally stable optically active PAIEUs based on a new reaction component, BPABTL. It was shown that, the temperature of 85°C and the reaction time of 2 h gives the highest viscosity for any PEG molecular weight. It means that, in spite of what we assumed, the constructed correlation in this study shows there is no significant difference between the viscosities of polymers based on different molecular weights of PEGs. As PUs are important class of polymers with a wide range of properties and applications, and there are variety of complicated parameters that affect the efficiency of the polymer chain growth, viscosity, solubility, physical, thermal and their mechanical properties, correlation methods can offer a fast and convenient route for the optimization of reaction conditions with respect to the desired property and application.

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#### REFERENCES

- Sharaf M.A., Illman D.L., Kowalski B.K. *Chemometrics*, Wiley InterScience, New York, Ch. 2 and 7, 1986.
- Wiggins M.J., Anderson J.M., Hiltner A. Biodegradation of polyurethane under fatigue loading, *J. Biomed. Mater. Res.*, 65A, 524-535, 2003.
- Sarti A., Foresti E., Zaiat M., Evaluation of a mechanistic mathematical model of a packed-bed anaerobic reactor treating waste water, *Latin. Am. Appl. Res.*, 34, 127-132, 2004.
- Rein G., Amnon Bar-Ilan A., Fernandez-Pello A.C., Ellzey J.L., Torero J.L., Urban D.L. Modeling of one-dimensional smoldering of polyurethane in microgravity conditions, *Symp. Combustion, 30th Int.*, 30, 2327-2334, 2005.
- Kukreja T.R., Kumar D., Prasad K., Chauhan R.C., Choe S., Kundu P.P., Optimization of physical and mechanical properties of rubber compounds by response surface methodology-two component modeling using vegetable oil and carbon black, *Eur. Polym. J.*, 38, 1417-1422, 2002.
- 6. Deming S.N., Morgan S.L. *Experimental Design*, Elsevier, Ch. 11, 1988.
- 7. Masao D., Material modeling platform, *J. Comput. Appl. Math.*, **149**, 13-25, 2002.
- Peng S., Fuchs A., Transport modeling and thermophysical properties of cellular poly(urethane-isocyanurate). Research report: Chemical Engineering, University of Nevada, Reno, Reno, NV 89557, unr.edu/homepage/afuchs/paper1.pdf and unr.edu/homepage/afuchs/paper2.pdf.
- Balasundaram B., Butenko S., Trukhanov S. Novel approaches for analyzing biological networks, *J. Comb. Opt.*, **10**, 23-39, 2005.
- Belgium L., Cerrolaza M., Computational modeling of tissue surgery, Zeman M.E. (Ed.), Venezuela, *Series: Adv. Bioeng.*, 1, www.witpress.com, 2005.
- Hamerton I., Herman H., Mudhar A.K., Chaplin A., Shaw S.J., Multivariate analysis of spectra of cyanate ester/bismaleimide blends and correlation with properties, *Polymer*, 43, 3381-3386, 2002.
- 12. Sadeghi R., New local composition model for polymer solutions, *Polymer*, **46**, 11517-11526,

Iranian Polymer Journal / Volume 16 Number 1 (2007)

27

2005.

- 13. Saunders J.H., Frisch K.C., *Polyurethane Chemistry. Part I*, Wiley InterScience, New York, Ch. 6, 1962.
- Legg N.R., Holden E., Schroeder H.E., *Thermoplastic Elastomers*, Meckel W., Goyert W., Wider W. (Eds.), Hanser, Munich, Ch. 2, 1987.
- Sanchez-Aduar M.S., Papon E., Villenave J.J., Properties of thermoplastic polyurethane elastomers chemically modified by rosin, *J. Appl. Polym. Sci.*, 82, 3402-3408, 2002.
- 16. Zha L., Wu M., Yang J., Hydrogen bonding and morphological structure of segmented polyurethanes based on hydroquinone-bis(*p*hydroxyethy)ether as a chain extender, *J. Appl. Polym. Sci.*, **73**, 2895-2902, 1999.
- Yang C.P., Lin J.H., Hsiao S.H., Synthesis and properties of aliphatic-aromati poly(amide-imide)s from sulfonyldianilines and *N*,*N*'-bis(ω-carboxyalkyl) pyromellitimides., *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 1175-1182, 1991.
- Harris R., Habermann C.E., Specialty polyurethane soft segments. III. Synthesis and characterization of *N*-isopropyl polyether polyamine oligomers containing backbone urea or amide moieties, *J. Appl. Polym. Sci.*, 46, 1561-1572, 1991.
- Woo E.J., Farber G., Farris R.J., Lillya P.C., Chien J.C.W., Structure-property relationships in thermoplastic elastomers: segmented polyetherpolyurethanes, *Polym. Eng. Sci.*, 25, 834-840, 1985.
- Sanchez-Aduar M.S., Papon E., Villenave J.J., Influence of the synthesis conditions on the properties of thermoplastic polyurethane elstomers, *J. Appl. Polym. Sci.*, **76**, 1590-1595, 2000.
- Sanchez-Aduar M.S., Papon E., Villenave J., Influence of the prepolymerization on the properties of thermoplastic polyurethane elastomers. Part 1. Prepolymer characterization, *J. Appl. Polym. Sci.*, **76**, 1596-1601, 2000.
- Sanchez-Aduar M.S., Papon E., Villenave J., Influence of the prepolymerization on the properties of thermoplastic polyurethane elastomers. Part II. Relationship between the prepolymer and polyurethane properties, *J. Appl. Polym. Sci.*, 76, 1602-1607, 2000.

- Murata H., Sanda F., Endo T., Synthesis and radical polymerization of a novel acrylamide having an α-helical peptide structure in the side chain, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1679-1682, 1998.
- Sanda F., Endo T., Synthesis and cationic polymerization of a novel optically active vinyl ether with *L*-proline structure, *Macromol. Chem. Phys.*, **198**, 1209-1216, 1997.
- Methenitis C., Morcellet J., Morcellet M., Polymers with amino acids in their side chain: Conformation of poly(*N*-methacryloyl-methionine), *J. Polym. Sci. Part A, Polym. Chem.*, 33, 2233-2239, 1995.
- Murata H., Sanda F., Endo T., Synthesis and functions of polymers based on amino acids, *Macromolecules*, **30**, 2902-2906, 1997.
- 27. Mallakpour S., Rafiemanzelat F., Synthesis and characterization of new optically active poly(amide-imide-urethane) thermoplastic elastomers, derived from bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine and polyoxyethylene-MDI, *React. Funct. Polym.*, **62**, 153-157, 2005.
- 28. Mallakpour S., Rafiemanzelat F., Synthesis and properties of novel optically active poly(amide imide urethane) thermoplastic elastomers by the reaction of a *l*-leucine based-diacid chain extender and PEG-terminated MDI., *Iran. Polym. J.*, **14**, 169-180, 2005.
- 29. Mallakpour S., Rafiemanzelat F., New optically active poly(amide-imide-urethane) thermoplastic elastomers based on the reaction of different PEGs, MDI, and a diacid based amino acid by two step method under microwave irradiation, *J. Appl. Polym. Sci.*, **98**, 1781-1792, 2005.
- 30. Mallakpour S., Rafiemanzelat F., Synthesis and characterization of novel optically active poly(ether-urethane)s modified by copoly(amideimide) segments based on amino acid through diisocyanate route: Influence of reaction parameters, *Iran. Polym. J.*, **15**, 79-90, 2006.
- 31. Mallakpour S., Rafiemanzelat F., Facile and rapid synthesis of novel optically active poly(amideimide-urethane)s derived from bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine and polyoxyethylene-MDI under microwave irradiation, *Iran. Polym. J.*, **14**, 909-919, 2005.

- Mallakpour S., Khoee S., Synthesis and characterization of new optically active poly(amide-imide urethane) thermoplastic elastomers, derived from 4,4-(hexafluoroisopropylidene)-*N*,*N*-bis(phthaloyl -*L*-leucine-*p*-aminobenzoic acid) and PEG-MDI, *J. Appl. Polym. Sci.*, **91**, 2288-2294, 2004.
- Mallakpour S.E., Hajipour A.R., Vahabi R., Synthesis and characterization of novel poly(amide-imide)s based on bis(p-amidobenzoic acid)-*N*-trimellitylimido-*L*-leucine., *J. Appl. Polym. Sci.*, 84, 35-43, 2002.