Macromol. Symp. **2006**, 241, 51–59 DOI: 10.1002/masy.200650908

Novel Polyurethane Gels: The Effect of Structure on Gelation

Pralay Maiti,[1] Ganga Radhakrishnan,[2] Palanisamy Aruna,[2] Goutam Ghosh[3]*

Summary: Novel polyurethane gels have been reported in common solvent like dimethyl formamide (DMF). Polyurethanes have been synthesized from diisocyanates, diols and rigid chain extenders. We have illustrated the influence of chemical structure of the chain extenders on gelation rate, thermal property and morphology of the gels in DMF. Gelation rate increases significantly with the rigidity of the chain extender. Introduction of more rigid chain extender molecules in polyurethane prepolymer enhanced the thermal stability of the pure polymer. On the contrary, the solvent retention power of the gels gradually decreases with increasing rigidity of chain extender presumably because of the poor dispersion/greater aggregation of the hard segments in the soft segment matrix. Morphology and formation of gelation have been discussed.

Keywords: chain extender; gelation; morphology; polyurethane; thermal properties

Introduction

Polyurethane (PU) is a unique material that offers the elasticity of rubber combined with the toughness and durability of metal. Compared to plastics, polyurethanes offer superior impact resistance, while offering excellent wear and elastic properties. Because urethane is available in a very broad hardness range, it allows one to replace rubber, plastic and metal with the ultimate in abrasion resistance and physical properties like shock absorber, sound/vibration dampening, soft electrical insulation, weather resistance etc. Polyurethane is a group of polymers and can be prepared by condensation polymerization of diisocyanates and diols (polyols) to form the prepolymers. Prepolymers are further polymerized in presence of another diol, so called chain extenders. Various types of diisocyanates, diols and chain extenders can be used to prepare different categories of polyurethanes. The reaction between diisocyanate of prepolymers and diol of chain extenders constitutes the hard segments in PU and soft segments come from the comparatively high molecular weight of diol. PU forms multiphase structures owing to the thermodynamic incompatibility between hard and soft segments.[1–4] Besides incorporating the urethane linkages these materials contain several other types of linkages like amide, urea, ether and esters.[5] The applicability of PU will be more if it is possible to prepare its gel in suitable solvent for the possible use in biomedical and leather industries. Unfortunately, commercial PUs do not form gel in most solvents. There are two possible ways to make PU gels 1) synthesizing through chemical route 2) to find out suitable medium to prepare gels. The gelation of different polymers is of current interest due to its wide applications. The mechanism of thermoreversible gelation and its properties have well been studied for past two decades.[6–10] So far, there is no report of polyurethane gel in the literature, though PU is being used for many applications.

---

[1] School of Materials Science and Technology, Banaras Hindu University, Varanasi 221 005, India
Fax: (91) 542 236 8707
E-mail: pralay_maiti@yahoo.com
[2] Polymer Science Division, Central Leather Research Institute, Adyar, Chennai 600 020, India
[3] UGC-DAE Consortium for Scientific Research, Bhabha Atomic Research Centre, Mumbai 400 085, India

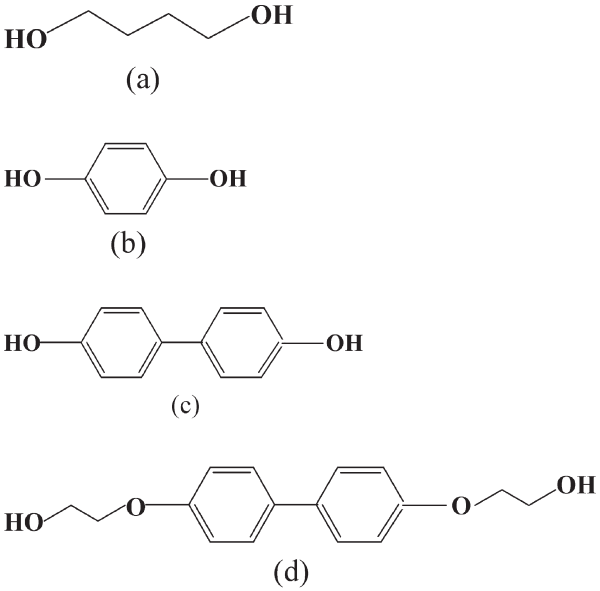
In this study we have synthesized PU with various diisocyanates, diols and chain extenders by two steps bulk polymerization technique. The resulted polymers are resemble commercial ones but with different chemical nature. Our approach was to prepare novel PU which will form gels in common solvents, keeping its strength and toughness like commercial PU. We have also varied soft segment content based on ether or ester-based diol to study the gelation behavior. Further, we have studied kinetics of gelation of modified polymer as a function of chain extender, hard segment content in different solvents. Thermal and morphological studies have also been done and finally, we established the plausible mechanism of gelation.

Experimental

Materials

The segmented polyurethanes used in this study were prepared by two-steps bulk polymerization process. The soft segment was either poly(tetramethylene oxide) glycol (PTMG, $M_w = 2900$, Aldrich) or polycaprolactone diol (PCL, $M_w = 1250$, Aldrich). The hard segment was either hexamethylene diisocyanate (HMDI) or $4,4'$-diphenylmethane diisocyanate (MDI) or tolylene diisocyanate (TDI). MDI (procured from Aldrich) was melted at 50 °C, the white solid was removed by filtration and the filtrate was cooled to yield pure monomer, which was used for further reaction. TDI and HMDI were used as received (procured from Aldrich). The chain extenders were butanediol (BD), hydroquinone (HQ), $4, 4'$ biphenol (BP) and $4,4'$ bis(hydroxyethyl) biphenol (HEBP). Chemical structures of the chain extenders have been shown in Scheme 1. The solvent used for gelation was distilled dimethyl formamide (DMF). HEBP was synthesized by refluxing BP and bromoethenol in slight basic medium in acetone. The reaction mixture was poured into water, filtered and the compound was purified by recrystallization from ethanol.

Synthesis of polyurethanes: A mixture of diol and and diisocyanate were taken in a



Scheme 1.
Chemical structure of different chain extenders (a) butanediol (BD) (b) hydroquinone (HQ) (c) biphenol (BP) and (d) bis(hydroxyethyl biphenol) (HEBP).

three necked flask fitted with a nitrogen inlet and a mechanical stirrer. The reaction mixture was heated at 70 °C for 3 h. Then the reaction mixture was cooled to room temperature, the pre-polymer was diluted with dimethyl formamide (DMF) and the chain extender dissolved in DMF was added drop wise. After completion of addition, few drops of dibutyl-tin-dilaurate (DBTDL) in toluene solution was added and the temperature was slowly raised to 70 °C and the reaction was conducted till the NCO peak around 2250–2270 cm^{-1} disappeared completely when examined with IR spectrometer. The polymer was then precipitated by pouring the reaction mixture into water, washed well with water and methanol and dried under vacuum. The amount of hard segments in PU was varied by introducing appropriate mole fraction of diisocyanate and diol. The GPC measurements were performed on pure PU with Waters GPC with DMF as the solvent at 70 °C. The calibration curves for GPC were obtained by using polystyrene standards. The molecular weight (M_w) of all PUs is in the range of 2.2×10^4 to 2.6×10^4 with polydispersity index between 1.2 to 1.5.

Preparation of gel: The gels were prepared in test tubes by taking appropriate amounts of polymer and solvent. They were sealed under vacuum (10^{-3} mm) by freeze thaw technique. They were homogenized at 80°C for 15 min and quenched to room temperature (30°C) to prepare the gel.

Gelation kinetic study: The kinetics of gelation was studied by using test tube tilting method.[11–15] The gelation time (t_{gel}) was considered as the time when no flow occurs after the sealed tube is tilted.[16–19] The accuracy of the gelation time measurement was ±10 s by trial and error procedure of repeated measurements. We compared the gelation time by using light scattering technique (the details studies are undergoing) and it is also reflected that the gelation time is almost the same than that we obsered by using test tube tilting method specially in the case of fast gelation kinetics.

Thermal characterization: Thermogravimetric analyses were done using TGA 951, Dupont, at the heating rate of 10°/min both for solid polymers and gels to know the decomposition temperature and solvent retention power, respectively. Differential Scanning Calorimetric traces were obtained by using a differential scanning calorimeter, (DSC 910, Dupont) at the heating rate of 5 °C/min to measure the glass transition temperature (T_g) of the solid polymers.

Morphology

Transmission electron microscopy (TEM) was used to observe the distribution of hard segments on soft segments of PU. TEM images were obtained using a Phillips instrument operated at an accelerating voltage of 100 kV. Dilute solution of PU was poured into the carbon-coated grid and was dried under vacuum for few days to evaporate solvent completely.

Results and Discussions

The rate of gelation was measured by test tube tilting method when the flow ceases. Figure 1 shows the hard segment content dependency on the gelation rate. For particular diol and diisocyanate, we observed increased gelation rate for higher hard segment content in PU. We have varied the type of diol, in one case it is ether diol (PTMG) and in other case it is ester-diol (PCL). Anyway, in both the cases, we observed higher gelation rate with increasing hard segment content. If the hard segment content is less than 20%, it does not form gel in the time frame we observed. The upper limit of time we observed for gelation to occur is 50 hrs. In both ether and ester diol, especially at high segment content, we observed a threshold zone as usual. Figure 2 exhibits the gelation rate as a function of concentration of PU, where the chemical nature of hard segment has varied from BD → HQ → BP to HEBP. The extent of hard segment was kept contant (around 50%) for all PU samples. Here, we observed the gelation rate to increase in the order of $BD < HQ < BP < HEBP$. At first sight we see that the

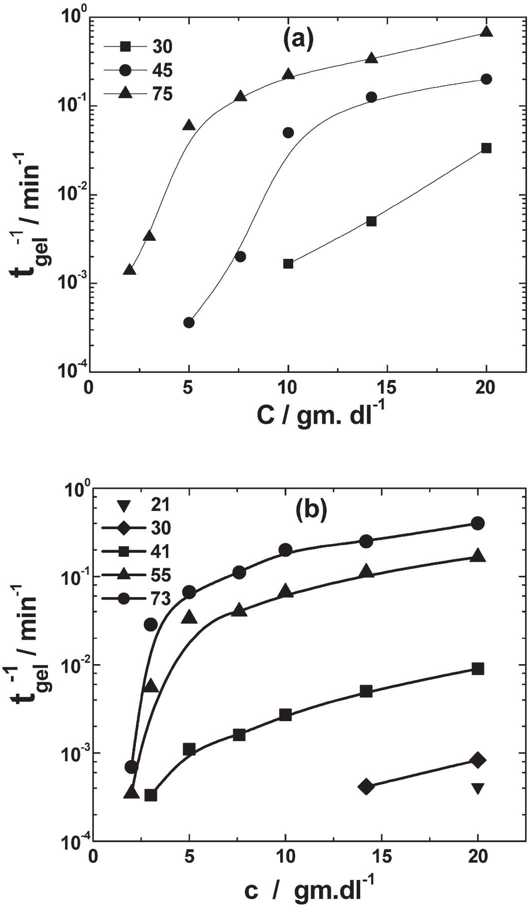


Figure 1.
Plots of gelation rate (t_{gel}^{-1}) versus polymer concentration in DMF (a) polytetramethylene glycol, (b) polycaprolactone (PCL) as diol. The numbers indicate the percentage of hard segment content in the polymer. In the both cases hexamethylene diisocyanate (HMDI) and biphenol (BP) were used for polymerization.

chemical complexity/rigidity of different hard segment also increases in the same order. That may provide us a first hand clue why the gelation rate increases in that particular order. Figure 3 compares the gelation rate between ether and ester-based diol, keeping the diisocyanate, chain extender and hard segment content of overall PU intact. For a particular chain extender, the gelation rate for ether diol is higher compare to ester diol but as in previous case the gelation rate increases with the order of BD < HQ < BP < HEBP both for ether and ester diol. Here, the hard segment content was kept constant for all PUs irrespective of ether or ester diols. Thermal behaviour: TGA curves (Fig. 4(a)) show the nature of degradation of solid polymer with different hard segment content in inert atmosphere. The degradation starts at 250 °C and the behaviour is bimodal. It is well known that hard segment content of PU degrades at lower temperature compare to soft segment part. Hence, for a particular system, with increasing hard segment concentration the degradation occurs at much lower temperature even though the initial decomposition starts at almost same temperature. Same behaviour was observed for all other systems having different diisocyanates, diols and chain extenders. If we vary the chain extenders, the degradation tempera-

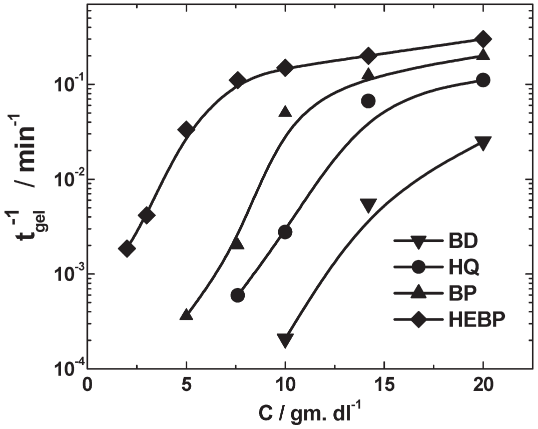


Figure 2.
Gelation rate (t_{gel}^{-1}) versus polymer concentration in DMF showing the dependence of chemical structure of chain extender on the gelation rate. The indicated symbols are the chain extenders used for polymerization. The hard segment content of all polymers is kept constant around 50%. The symbols are as usual used in the text.

ture increases in the order of BD < HQ < BP < HEBP (Fig. 4(b)). With the increase of rigidity of chain extenders the decomposition temperature was enhanced to a significant level, more than 100°C. TGA experiments on gels indicate that solvent molecules goes off first and finally the polymer degrades at the same temperature in which solid PUs start degrading. But the solvent molecules evaporate first for most rigid chain extender and the order of solvent retention power is HEBP < BP < HQ (Fig. 4c).

Figure 5 represents the DSC traces for the PUs polymerized with different chain extenders but the hard segment content was kept constant at 50%. Here we observed that glass transition temperature (T_g) increases in the order of HEBP < BP < HQ < BD, the reverse trend of gelation

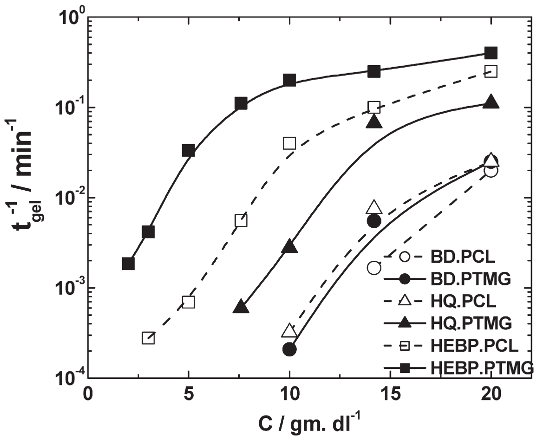


Figure 3.
Plot of gelation rate (t_{gel}^{-1}) versus polymer concentration in DMF. The effect of two different diols (PCL and PTMG) on gelation rates. The open symbols are for the polymers containing PCL as diol and filled symbols are for the polymers having PTMG as diol. Different chain extenders are mentioned with the diol. The hard segment content of all polymers is kept constant around 50%.

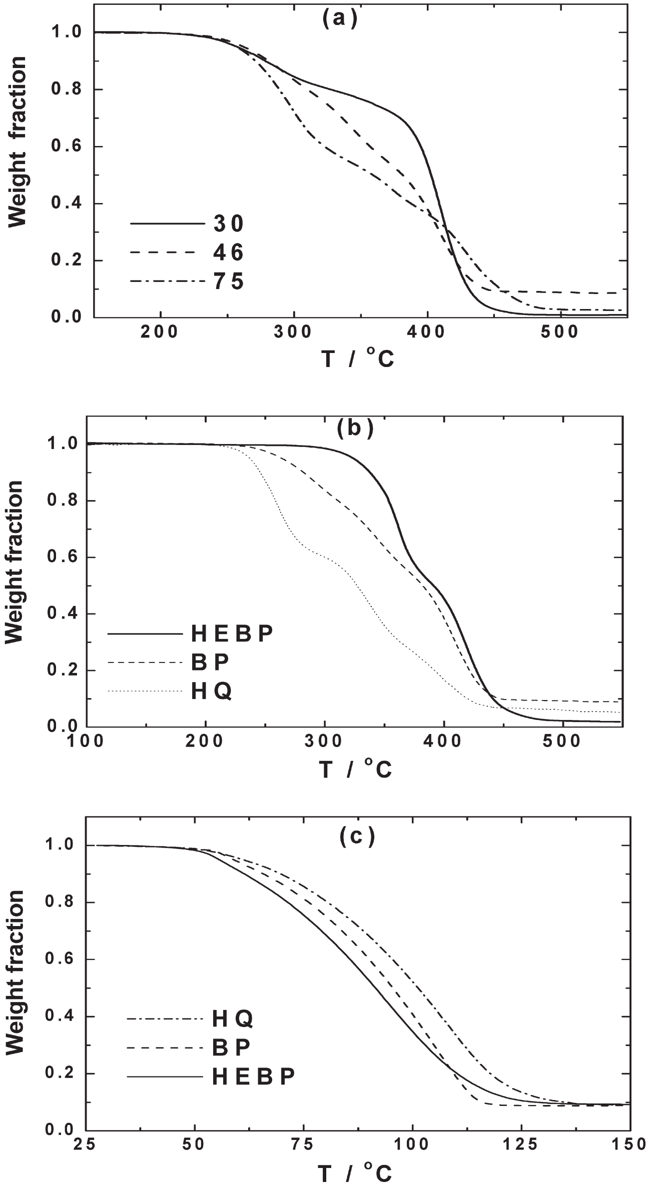


Figure 4.

TGA curves of different PUs, (a) pure polymers with different hard segment content PU, (b) pure polymers with various chain extenders and hard segment was kept constant at 50% and (c) solvent retention power of gels, PU with different chain extenders.

rate. On the contrary, for a particular chain extender T_g increases with increasing hard segment content (not shown in the figure).

It is well known that commercial PUs do not form gels. We have tested some of PU available (Bayer's PU) in the market but they do not form gel in any solvents we have tested including DMF. Commercial PUs are made of TDI or MDI as diisocyanate, PTMG / PCL as soft segment and mostly BD as the chain extender. We took simple HMDI as diisocyanate and rigid chain extenders like BP and HEBP. Fortunately, with modified rigid chain extenders, PU

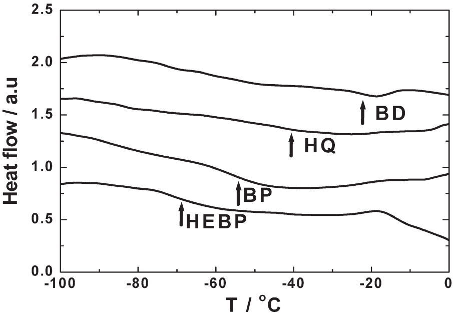


Figure 5.
DSC curves for solid polyurethanes containing different chain extenders as mentioned in the figure. The hard segment content of all polyurethanes is kept constant around 50%.

forms gel in DMF. We have also synthesized PU with MDI or TDI as diisocyanate and BP or HEBP as chain extenders. Still they also do not form gels in DMF. Apparently, HMDI along with rigid chain extenders are mainly responsible for the formation of gels in solvent like DMF. Most of the synthesized PU have molecular weight in the range of 2.5×10^4, so the effect of molecular weight is nullified and in fact the commercial PUs have higher molecular weight compare to synthesized PUs.

The molecular reason for the formation of hard segment, so called segmented PU, is because of the intermolecular interaction through hydrogen bonding (H-bonding) and this region is often agglomerated and crystallized in solid polymer too. The gelation rate of PU was increasing with hard segment content both for ether and ester diols. The hard segments are mainly responsible to make physical crosslinking point or junction through which networking or formation of gel is enhanced. Furthermore, if we increase the rigidity or the length of chain extender, say from BD to HEBP, there may be two possibilities 1) extent of formation of H-bonding and 2) the overall length of segmented zone. Anyway, PU with BP or HEBP as chain extender has got better segmented zone and as a result produces gel within short period of time compare to PU having BD or HQ as chain extender. This will be more clear when thermal or solvent retention power of gel will be discussed. For a particular system of diisocyanate and chain extender, PU with ether diol (PTMG) has higher gelation tendency vis-a-vis ester diol (PCL). Ester linkages in PCL are more polar, as compared to ether group in PTMG, and reside only in soft zone in PU and therefore, interact with solvent

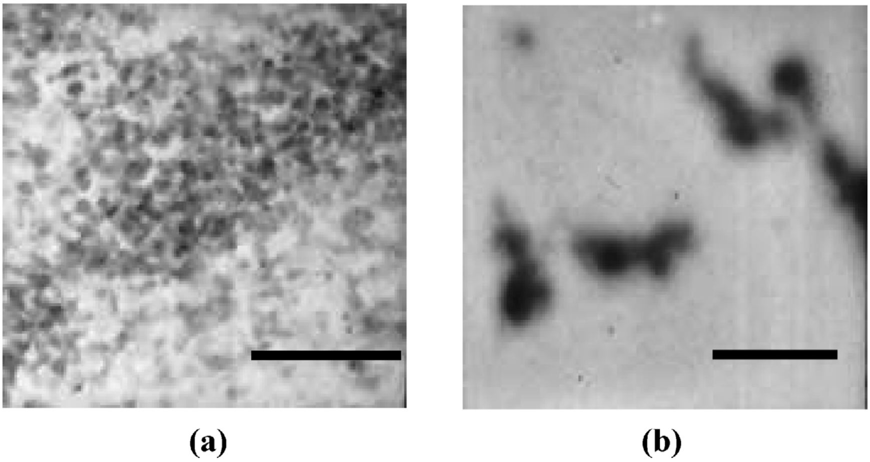


Figure 6.
TEM bright field images of polyurethanes with (a) BD and (b) HEBP as chain extender, showing the distribution of hard segments over soft segments.

throughout the entire chain as a competitive process. While in PTMG, the interaction occurs only through hard segment zone as result, formation of gel is bit faster in PTMG case.

Thermal degradation behaviour of PU is bimodal and low temperature degradation corresponds to the decomposition of hard segments and second step degradation is due to the decomposition of soft segments.[20,21] As the rigidity of the chain extender increases from BD to BP or HEBP, maintaining the hard segment content constant, then PU chains become stiffer, as a result thermal decomposition temperature increases. On the contrary, the solvent rentention power decreases with the rigidity of the chain extenders. To have a look into that we conducted TEM experiment for PU with BD and HEBP as chain extenders. It is very clear from the micrographs (Fig. 6) that in BD, the hard segmented zone are small and dispersed into the soft segment part. On the other hand, in HEBP, the hard segments are obviously large but quite separated from each other. As in BD case the hard segments are distributed nicely and the solvent has less chance to go out under thermal treatment while there are enough space between the hard segmented zone in HEBP, and hence, solvent can move easily through those channels. With the help of this morphological behaviour we can explain why the T_g of HEBP is lower than that of BD system. Soft segmented zones in HEBP or any other stiffer configuration of chain are enough large and can relax easily at low temperature, while in BD case, hard segment zones are dispersed nicely and make the whole system a rigid one and thus T_g of BD is the highest amongst other chain extenders and follow the order of $BD > HQ > BP > HEBP$.

Conclusions

We have synthesized novel polyurethanes with different kinds of chain extenders such as biphenol and bis(hydroxyethyl biphenol) using hexamethylene diisocyanate and polytetramethylene or polycaprolactone as soft segments. The modified polyurethanes form gels in common solvent like dimethyl formamide. The gelation kinetics have been measured which exhibit higher gelation rate for the polyurethane containg more rigid chain extenders. The thermal property improves with the rigidity of the chain extenders. The solvent retention power of polyurethane having rigid chain extenders decreases slightly as the gap between the hard segments increases. The glass transition temperatures also follow the same trend. We shed light onto the morphology and formaton of gel in solvent, providing a suitable mechansim.

Acknowledgement: The authors acknowledge Prof. O. N. Srivastava, Department of Physics, Banaras Hindu University for the morphological (TEM) studies.

[1] P.E. Gibson, M.A. Vallence, S.L. Cooper, In "*Developmet in Block Copolymers*"; I. Goodman ed.; Applied Science Series; Elsevier;London, 1982, p217.

[2] S.L. Cooper, A.V. Tobolsky, *J. Appl. Polym. Sci.* **1966**, 10, 1837.

[3] R.W. Seymour, S.L. Cooper, *J. Polym. Sci., Polym. Lett. Ed.* **1971**, 9, 689.

[4] Y. Li, T. Gao, J. Liu, K. Linliu, C.R. Desper and B. Chu, *Macromolecules* **1992**, 25, 7365.

[5] R. Herrington and K. Hock, "*Flexible Polyurethane Foams*", 2ndEd. Dow Chem. Co. 1998.

[6] J.M. Guenet, "*Thermoreversible gelation of polymers and biopolymers*"; Academic Press; London, 1992.

[[7] "*Reversible polymer gels and related systems*" P.S. Russo, Ed.; ACS Symposium Series; American chemical society: Washington DC, 1986.

[8] H. Berghmams, In "*Integration of Fundamental Polymer Science and Technology*" P.J. Lemstra, L.A. Kleintjens, Eds.; Elsevier Applied Science; London; 1988, 2, 296.

[9] K. Te Nijenhuis *Adv. Polym. Sci.* **1997**, 130, 1.

[10] D. Asnaghi, M. Giglio, A. Bossi, P.G. Righetti, *J. Chem. Phys.* **1995**, 102, 9736.

[11] S. Mal, P. Maiti, A.K. Nandi, *Macromolecules* **1995**, 28, 2371.

[12] S. Mal, A.K. Nandi, *Polymer* **1998**, 30, 6301.

[13] A.K. Dikshit, A.K. Nandi, *Macromolecules* **1998**, 31, 8886.

[14] H.M. Tab, A. Hiltner, A. Moet, E. Baer, *Macromolecules* **1983**, 16, 28.

[15] A. Prasad, L. Mandelkern, *Macromolecules* **1990**, 23, 5041.
[16] D.J. Abdallah, R.G. Weiss, *Langmuir* **2000**, 16, 352.
[17] J.W. Cho, H.Y. Song, S.Y. Kim, *Polymer* **1993**, 34 1024.
[18] J.W. Cho, G.W. Lee, *J. Polym. Sci.* **1996**, B34, 1605.
[19] M. Ohkura, T. Kanaya, K. Kaji, *Polymer* **1992**, 33, 5044.
[20] L.H. Sperling, *Polym. Eng. Sci.* **1986**, 26, 517.
[21] E.G. Bajsic, V. Rek and and A. Agic, *J. Elast. Plast.* **2003**, 35, 311.