

Temperature-sensitive star-branched poly(ethylene oxide)–*b*-poly(propylene oxide)–*b*-poly(ethylene oxide) networks

Lev Bromberg*

Center for Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

(Received 2 September 1997; revised 17 November 1997; accepted 9 December 1997)

Temperature-sensitive polyurethanes are obtained by reacting trifunctional isocyanate with poly(ethylene oxide)–*b*-poly(propylene oxide)–*b*-poly(ethylene oxide) [Pluronic L122]. The temperature-dependent interactions among poly(propylene oxide) [PPO] segments are observed by n.m.r. At low polyurethane concentrations, segment–segment PPO interactions within a given gel cluster are predominant, whereas above the concentration threshold, interparticle interactions lead to the aggregation of clusters. The formation of physical networks in polyurethane suspensions with the temperature increase is followed by the appearance of temperature- and shear-thinning viscoelastic gels. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyurethanes; poly(ethylene oxide)–*b*-poly(propylene oxide)–*b*-poly(ethylene oxide); gels)

INTRODUCTION

Amphiphilic polymers composed of hydrophobically modified hydrophilic segments have drawn attention primarily due to their associative properties in aqueous solutions^{1–6}. Polymers with poly(ethylene oxide) [PEO] arms and a core consisting of hydrophobic tri- or tetraisocyanate were shown to possess associative properties when the PEO arms were modified with hydrophobic nonylphenoxy end groups^{1,2}. These self-assembling copolymers with hydrophobic cores form aggregates above their critical micelle concentrations, which depend on the size of the core. Typically, the concept of a hydrophobe used for modification of a hydrophilic, water-soluble polymer implies extreme hydrophobicity of the former, which is either a hydrocarbon or fluorocarbon^{8,9}. The lifetimes of the associations arisen between these hydrophobes, which are water-insoluble at any temperature, decrease exponentially as the temperature increases¹⁰. This is consistent with the usual result of the Arrhenius-like decrease of zero shear viscosity in the hydrophobe-modified ethoxylated urethane (HEUR) polymers¹¹. On the other hand, since hydrophobic interactions are driven by the entropy of the system, the number of associations (and thus the viscosity) are increasing with a rise in temperature. Why the lifetime of associations is the overriding factor suppressing the effect of their number⁹ is not obvious. Neither is it well understood why, e.g. some fluorocarbon-associating polymers show maxima on the viscosity *versus* temperature plots^{9,12}. In the present work, we address the problem of the associating polymers with complex temperature dependencies of viscosity by introducing a concept of poly(propylene oxide) [PPO] blocks as a hydrophobe. The transfer energy of the CH(CH₃)CH₂O group from the aqueous to micellar phase was found to be four times smaller at room

temperature than the corresponding energy for a CH₂ group¹³. A relatively large area of ethylene oxide units in PEO–PPO–PEO block-copolymer compared to that in the hydrocarbon-ethylene oxide (C₁₂EO₈) may be a consequence of a weaker hydrophobic effect with PPO in the core than with hydrocarbon chains, which allows for a larger water-exposed interfacial area¹⁴. The relative ‘hydrophilicity’ of PPO and its extremely temperature- and chain length-dependent interactions with water^{15–17} allow for the design of PPO-containing block-copolymers with temperature-dependent viscosities of their aqueous solutions^{13,18}. Triblock PEO–PPO–PEO copolymers, known under the trade name Pluronic®, available in a variety of lengths and PPO/PEO ratios are particularly interesting with this regard, as their rheological properties are extensively studied. Thermoviscosification and gelation in aqueous Pluronic solutions is a well-documented phenomenon related to the formation of lyotropic liquid crystalline phases above micellization temperatures^{19–21}. Temperature-dependent formation of micelles in these solutions is due to entropy-driven aggregation of the PPO segments in Pluronic. Cross-linked hydrogels derived from Pluronic surfactants by either random intermolecular cross-linking induced by high energy γ -irradiation^{22,23}, or by modifying both ends of the Pluronic molecule with an acryloyl group following free-radical polymerization^{24,25}, were shown to form multicomponent structures dependent upon both the compatibility between hydrophilic and hydrophobic segments and the colloidal properties of the individual molecules. The nature of the gels formed from acryloyl-modified Pluronic remains unspecified, probably because of the abundant hydrogen-abstraction reactions in the Pluronic molds or solutions upon free-radical polymerization²⁶. The randomness of the cross-linking ought to make it hard to control the structure of the gels. Therefore, in order to obtain gels of well-defined structure, we have chosen a route of gel synthesis via end-linking of Pluronic with multifunctional cross-linkers. The chemistry of end-linking

* Current address: MediSense, An Abbott Laboratories Company, 4A Crosby Drive, Bedford, MA 01730, USA

of PEO developed for HEUR^{8,27} applies for the Pluronics, as they contain hydroxyl end-groups. In this work, we chose relatively hydrophobic and long-chain Pluronic L122 as a 'hydrophobically modified' arm, and tris(6-isocyanato-hexyl) isocyanurate ($\log P = 3.47$, hydrophilic surface area 51%) as a core in star-branched polymers. The experimental objectives of this work were: (i) to characterize the structure of the polymers depending on the ratio of hydroxyl and isocyanate functionalities preset in the reaction mixture; (ii) once cluster structures are formed, elucidate segment-segment interactions within a given gel particle and those between particles; and (iii) show formation of thermoreversible suspensions. Recently, Winter and Mours²⁸ emphasized that thermoreversible transitions in suspensions are complicated to study since they are accompanied by additional phenomena, e.g. order-disorder transitions of particulates, anisotropy, particle-particle interactions, Brownian motion and sedimentation-particle convection. It is believed that the present work may contribute to the understanding of such systems.

EXPERIMENTAL

Materials

Pluronic L122 (nominal molecular weight 5000, formula EO₁₂PO₆₇EO₁₂) was obtained from BASF. Pluronic was kept under vacuum (10⁻³ torr) at 50°C for 48 h and stored in sealed flasks under nitrogen. Equivalents of hydroxyl groups in dried Pluronic were determined by methods described elsewhere^{29,30}. 1,6-Diisocyanatohexane (Aldrich, 98%) was distilled under vacuum and stored under nitrogen prior to use. Tetrahydrofuran (Aldrich, anhydrous, 99.9 + %) was distilled under nitrogen from the purple sodium/benzophenone ketyl and was stored under nitrogen before use. All other chemicals were obtained from commercial sources and were of the highest purity available.

Syntheses

Tris(6-isocyanatohexyl) isocyanurate (TIHI) of 23 wt% NCO content and 99.6% purity was synthesized by trimerization of 1,6-diisocyanatohexane and purified as described elsewhere³¹.

The resins were synthesized as follows. To a flask containing a solution of rigorously dried 2.0 g Pluronic and 40 mg dibutyltin dilaurate (DBTDL) in THF, a weighed amount of TIHI was added under Drierite-treated argon. The amount of THF was set such that a 10 wt% Pluronic resulted in the reaction mixture. The flask was agitated, purged with argon and kept under reflux at 75°C for five days. The polymers were precipitated into petroleum ether and dried with a water aspirator. Purification was accomplished by repeated dissolution (or swelling) in THF and precipitation into petroleum ether. Polyurethanes were dried under vacuum for two-three days at 40°C until constant weights were maintained. The polymer was characterized by the initial ratio of equivalents of isocyanate and hydroxyl groups ($\rho = [\text{NCO}]/[\text{OH}]$) set for the synthesis. The critical mole ratio necessary to reach the gelation ($\rho_{\text{gel}} = 0.718$) was determined as the lowest ρ value where the THF-insoluble gel was obtained after synthesis at full conversion of the isocyanate groups^{32,33}.

Procedures

Dynamic light scattering experiments were performed on polyurethane samples in deionized water with a Spectra Physics He-Ne Model 127 laser operating at a scattering

angle of $\theta = 90^\circ$ and a wavelength of incident light of $\lambda = 633$ nm at a power of 50 mW. The scattering cell was thermostatted using a refractive index matching silicone oil, and temperature controlled to within 0.02°C. The intensity autocorrelation function $C^{(2)}(\tau) = \langle I(\tau)I(0) \rangle$ was measured on a Brookhaven BI 2030AT 136-channel digital correlator in a form³⁴ $C^{(2)}(\tau) = A[1 + \beta|c^{(1)}(\tau)|^2]$, where A is the experimentally found base line, β is the spatial coherence factor, and $c^{(1)}(\tau)$ is the electric field autocorrelation function. The analysis of the function $c^{(1)}(\tau)$ was done using the method of cumulants^{34,35}. The electric field autocorrelation function was presented as a sum of single exponentials

$$c^{(1)}(\tau) = \int_0^\infty C(\Gamma) \exp(-\Gamma\tau) d\Gamma$$

where $C(\Gamma)$ is the normalized distribution function of the decay rates and $\Gamma = D_z q^2$. Here D_z is the z -average translational diffusion coefficient and $q = (4\pi n_0/\lambda)\sin(\theta/2)$, the magnitude of the scattering vector³⁶. Hydrodynamic radii r_h were calculated from the D_z values using the Stokes-Einstein equation, $r_h = k_B T / (6\pi\eta D_z)$, where k_B and η are the Boltzmann constant and the solvent viscosity measured at the temperature T .

Suspensions of the THF-insoluble gels ($\rho > \rho_{\text{gel}}$) were made by cryogenic grinding of the dry polymer particles which were then dialysed against deionized water, homogenized and allowed to equilibrate with deionized water with a pH adjusted to 7.0. The effective mean size of the suspended particles was measured on a Coulter LS particle sizer. A Carl Zeiss Standard 25 microscope was used for direct particle observations.

Rheological properties of polyurethane, and Pluronic suspensions and solutions were assessed using a PC-equipped Brookfield LVDV-II + Digital Viscometer with a 2 ml thermostatted adapter (chamber dimensions, 12.70 mm diameter, 28.19 mm depth) and a SC4-14/6R spindle (8.74 mm diameter, 8.64 mm side length) adopting coaxial-cylinder geometry. The solution was loaded into an adapter cup and thermostatted at the desired temperature while measuring the viscosity at different shear rates. Shear rate (γ , s⁻¹) was found on the surface of the spindle. One hundred readings were averaged at each temperature.

Oscillatory shear experiments were done with a Rheolyst AR 1000 Rheometer (TA Instruments) equipped with two Peltier plates for temperature control. The angular frequency of oscillatory shear was 10 rad/s at 2% strain, the rate of temperature change 0.01°C/s. Cone and plate sample geometry (diameter, 4 cm; angle, 2°) was applied.

Gel-permeation chromatography was run at 15°C on a Shimadzu LC-10A Series HPLC system with a Viscotek SEC³ Triple Detector System, which included a differential Wheatstone bridge viscometer, differential laser refractometer and small-angle laser light scattering detector. Light scattering chromatograms were obtained with a small-angle light scattering photometer using a 10 ml scattering cell at the output of the columns. The incident light at a 6° scattering angle was supplied by the He-Ne laser. A similar scattering geometry was reported to be devoid of angular dependency of intensity scattered by molecules whose radius of gyration is less than about 250 nm³⁷. A 1.0 mg/ml sample of polymer solution in 0.05 M NaNO₃ (100 ml) was loaded onto a PL aquagel-OH 40,50 and 60 analytical temperature-controlled 3-column system (particle size 8 or 15 μm ; dimensions 300 mm \times 7.5 mm, Polymer Laboratories Inc.) and then eluted with 0.05 M NaNO₃ using a

pump speed of 1.0 ml/min. Prior to injection, each polymer solution was filtered through a nylon filter (pore diameter 0.45 mm).

Fractionation was performed at ambient temperature on a Hewlett Packard 1050 HPLC system with a small-angle laser light scattering detector. A 1.0 mg/ml polymer solution in tetrahydrofuran (100 ml) was loaded onto a PLgel preparative 3-column system (porosities, 50, 100, 500, 10³ and 10⁴ Å, particle sizes 10 mm, dimensions, 300 × 25 mm, Polymer Laboratories). The polymer fractions were dried under vacuum and subjected to GPC as described above.

In swelling experiments, resins of known dry weights (W_d) were placed in excess deionized distilled water and allowed to swell for five–15 days at the desired temperature until constant weights (W_s) were reached. The swelling degree was calculated by $S = (W_s/W_d - 1)$.

N.m.r. spectra of 10 wt% polymer solutions in D₂O were acquired on a Bruker AM300 spectrometer (proton and carbon resonances at 300.1 and 75.47 MHz, respectively) within 5–65°C. DEPT-135 ¹³C parameters were: 20 000 Hz spectral width, 3 or 5 Hz line broadening, 0.819 s acquisition time, number of scans 100 000 or more. Tetramethylsilane and dioxane were used as external frequency locks for ¹H and ¹³C n.m.r., respectively. In n.m.r. experiments, we concentrated only on the behaviour of the CH₃ group in PPO. The change in half-width of the signal of methyl protons at the high-field peak of the doublet at 1.1 ppm of poly(propylene oxide) block of Pluronic ($\Delta H_{1/2}$) and the percentage of the higher temperature chemical shift of the methyl carbons in ¹³C n.m.r. (CS) were used to characterize the temperature-dependent properties of polyurethanes^{38–40}. Infrared spectra of polymeric samples dispersed in KBr were recorded in a water-free atmosphere on a Perkin–Elmer Model 1600 spectrometer.

Typical spectral parameters of the polyurethanes were as follows. ¹H n.m.r. (D₂O, 20°C, $\rho = 0.716$): δ 4.2 (m, CH₂-O(C=O)R of Pluronic), 3.7 and 3.6 (m, CH₂-O of Pluronic), 3.4 (m, CH₂-N-C=O of isocyanurate), 1.5 (m, CH₂-C-NR₂ of isocyanurate), 1.1 (d, CH₃-R of PPO in Pluronic); ¹³C n.m.r. (D₂O, 20°C, $\rho = 0.716$): δ 184 (ester C=O), 158 (urea), 75.8, 73.6, 70.3 (ether C-O-C), 45.4, 44.9, 38.0, 36.6 (primary C-O and secondary C-C), 17.9 (CH₃ of PPO in Pluronic); IR (KBr, $\rho = 0.718$): 2933 (methyl C-H of PPO in Pluronic), 1713, 1685 (C=O in isocyanurate ring), 1452 (OC-NR-CO in isocyanurate ring), 1220 (ester C-O stretch), 1099 cm⁻¹ (antisym. and sym. COC stretch in Pluronic).

Lower critical solution temperatures (LCST) of polymer suspensions were determined at the onset of the absorbance increase with increasing temperature⁴¹. Absorbance at 500 nm was continuously monitored in a flow-through quartz cell (path length 0.2 cm) under controlled temperature conditions. The rate of temperature increase was 0.05°C/min.

RESULTS AND DISCUSSION

Polyurethane structure

The topology of starburst polymers has been the subject of a considerable amount of work over the last decade, starting from publications of Tomalia and co-workers^{42,43}. Drawing an analogy with the method of dendrimer synthesis by iterative steps⁴⁴, let us present the structure of polyurethanes as a result of the stepwise *in situ* construction of branch points around a single TIHI core (Scheme 1). The model structure in Scheme 1 predicts that, if no side

reactions are involved, the ratio of the isocyanate and hydroxyl groups preset in the reaction mixture (ρ) is related to the number of generations of the dendrimer structure (n) as follows:

$$\rho = \frac{1 + 3(2^{n-1} - 1)}{2 + 4(2^{n-1} - 1)}$$

Clearly, the range of ρ values that may yield our model structure is limited, since at large n , $\rho \rightarrow 0.75$. In fact, the appearance of glassy gels insoluble in THF (gelation threshold) was observed even earlier ($\rho_{\text{gel}} = 0.718$). This may be attributed to the intramolecular branching, cyclization and cross-linking via allophanate and urea bonding³¹, as well as intermolecular dendrimer bridging due to urea formation. These processes along with the isocyanurate trimerization³¹ may cause the appearance of an increasing number of imperfections in the starburst structure. It has been stressed⁴⁵ that the synthesis of a perfect polyurethane network is hardly accessible experimentally due to incomplete conversion of the functional groups. A further estimate of the degree of imperfection of the obtained polyurethane can be obtained from the comparison of the nominal and actual functionality of the Pluronic incorporated into the polyurethane. The actual weight-average functionality of the Pluronic (f_p) can be estimated from the critical ρ_{gel} values³². According to the Flory–Stockmayer theory^{46,47}

$$\alpha_{\text{OH}}\alpha_{\text{NCO}} = [(f_p - 1)(f_i - 1)]^{-1}$$

where α_{OH} and α_{NCO} are the molar conversions of the hydroxyl and isocyanate groups, respectively, into the urethane bonds, and $f_i = 3$ is the functionality of TIHI.

Since in our samples $\alpha_{\text{NCO}} \rightarrow 1$ and $\alpha_{\text{OH}} = \rho$, the functionality of Pluronic at gelation threshold is about $f_p = 1 + 1/2\rho_{\text{gel}} = 1.7$. Significant deviation of the obtained number from the nominal $f_p = 2$ indicates a substantial number of NCO groups in allophanate cycles without having reacted with the OH groups of Pluronic. A similar phenomenon was encountered in reactions of diisocyanates with triols in dilute ($\leq 20\%$) benzene solutions³².

When amounts of Pluronic and TIHI corresponding to the ρ approaching ρ_{gel} were preset in the reaction mixture ($\rho = 0.716$), a transparent viscous liquid without apparent

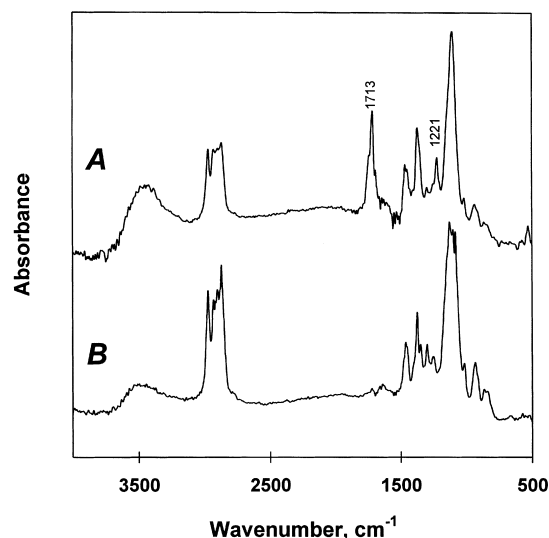
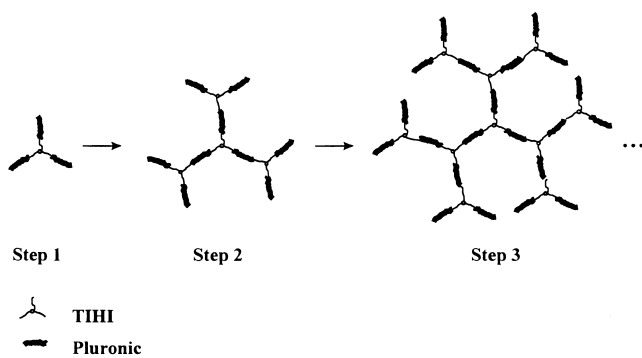
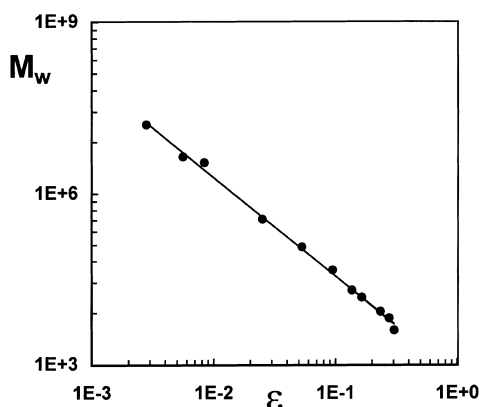


Figure 1 FTIR spectra of polyurethane synthesized by reacting stoichiometric amounts of Pluronic L122 and tris(6-isocyanato)hexyl isocyanurate (A) and original Pluronic L122 (B)



Scheme 1 Model of polyurethane network formation

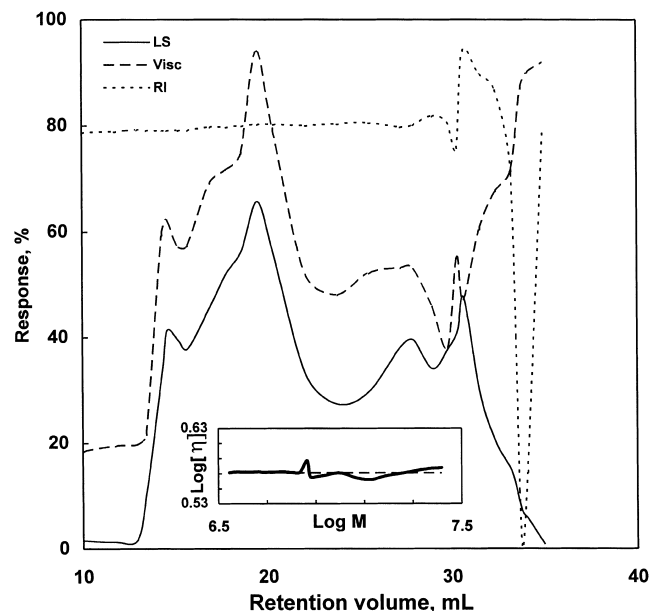

 Figure 2 Mean weight-average molar mass (M_w) of polyurethanes on the log–log scale as a function of the distance to the gel point ($\epsilon = \rho - \rho_{gel}/\rho_{gel}$)

phase separation was observed after the completion of the condensation reaction. FTi.r. (Figure 1) of the corresponding dry polymer shows no peaks at 2200 cm^{-1} , characteristic of a free isocyanate group, thus indicating completeness of the condensation reaction. When compared to the spectra of the original Pluronic, peaks at 1713 cm^{-1} (carbonyl in isocyanurate ring) and 1221 cm^{-1} (C–O stretching band corresponding to O–CH₂R group) clearly show the formation of polyurethane. A broad peak in the region 3600 cm^{-1} , although smaller in the polyurethane compared to unreacted Pluronic, indicates the presence of the OH end-groups on the polyurethane surface. On the other hand, no additional peaks in the amide region were observed, indicating that side reactions of urea formation^{48,49}, if any, were negligibly minor.

The mean weight-average molar mass (M_w) of polyurethanes obtained within the range $0.500 < \rho < 0.718$ is shown on the log–log scale in Figure 2 as a function of the distance to the gel point ($\epsilon = \frac{\rho - \rho_{gel}}{\rho_{gel}}$, as in Ref. 33). The power law obtained was

$$M_w = 6.5 \times 10^2 \times \epsilon^{-1.73} \text{ with } \gamma = 1.73$$

The obtained exponent γ is in excellent agreement with the $\gamma = 1.74$ predicted by the 3D percolation model^{50–53}. Mechanistically, this indicates that our polyurethane may be described as a system of fractal gel clusters (ensembles of connected bonds, Scheme 1) which become one giant cluster at a threshold ($\epsilon \rightarrow 0$). It is interesting to note that the range $\epsilon \leq 0.3$ used to obtain the scaling parameter γ was wider than $\epsilon \leq 0.1$ previously considered for polyurethanes^{32,33}, and yet a good correlation with the percolation theory^{33,53} was observed.


 Figure 3 A triple-detector chromatogram of polyurethane ($\rho = 0.716$). LS, Visc and RI stand for the light scattering, differential viscometer and refractive index detectors' outputs. The intrinsic viscosity ($[\eta]$) versus molecular weight log–log plot for the same sample is shown in the insert

A triple-detector chromatogram of a THF-soluble polyurethane ($\rho = 0.716$, Figure 3) afforded a weight-average molecular mass of 16.04×10^6 . Very large molecular weights and a polydispersity over 50 confirm that the system at hand was approaching the gelation threshold^{33,37,54}. Intrinsic viscosity versus molecular weight plot yielded a slope equal to 0 in logarithmic coordinates (insert in Figure 3). Consequently, the Mark–Houwink parameter^{55†} a was equal to 0. Assuming zero-shear conditions in the GPC experiment, one can apply the Einstein relation which links the viscosity η of a solution of hard spheres occupying a volume fraction Φ ⁵³:

$$\eta = \eta_0 \left(1 + \frac{5}{2} \Phi \right)$$

where η_0 is the viscosity of the solvent.

Since $\Phi = N_A C/M(4/3)\pi R_M^3$ and

$$[\eta] = \lim_{C \rightarrow 0} (\eta/\eta_0 - 1)/C,$$

the expression for the intrinsic viscosity becomes⁵⁶

$$[\eta] = \left(\frac{10}{3} \pi N_A \right) R_M^3/M$$

Here C , g/cm^3 , is the concentration of spherical macromolecules of radius R_M and molecular weight M , and N_A is the Avogadro's number.

Thus, since the intrinsic viscosity is independent of M (Figure 3), R_M^3 should vary linearly with M . The condition of $R_M^3/M = \text{constant}$ is characteristic for the starburst dendrimers with a radially symmetrical star-shaped architecture⁵⁷.

Temperature sensitivity

In dynamic light scattering experiments, the polyurethane prepared near the gelation threshold ($\rho = 0.716$) was

† Parameter a is defined from the Mark–Houwink equation $[\eta] = KM^a$, where h and K are intrinsic viscosity and a constant, respectively.

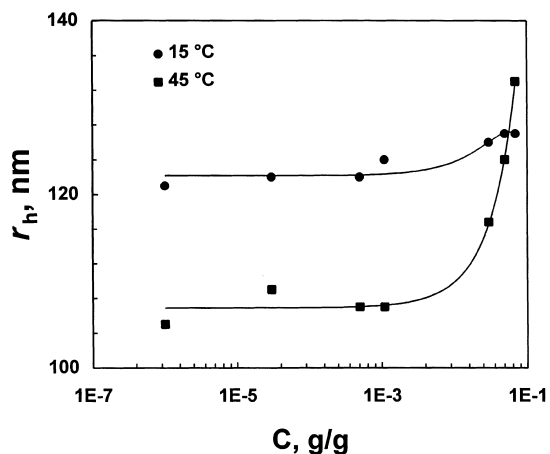


Figure 4 Effect of polymer concentration on hydrodynamic radii of the largest clusters of polyurethane³⁷ ($\rho = 0.716$) measured by dynamic light scattering in deionized water at 45 and 15°C

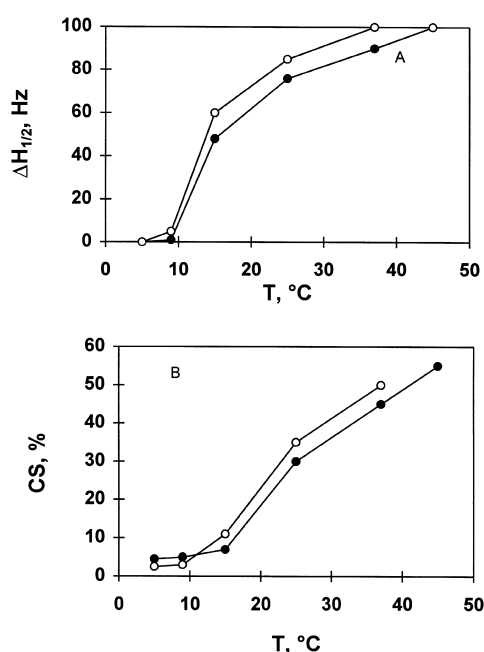


Figure 5 Effect of temperature on the half-width of the signal of methyl protons at the high-field peak ($\Delta H_{1/2}$) of the doublet at 1.1 ppm of poly(propylene oxide) block of Pluronic (A), and the percentage of the higher temperature chemical shift (CS) of the methyl carbons in ^{13}C NMR (B)

fractionated in the following way. The polyurethane solution in THF was run through the preparative GPC system and the fraction around the maximum in the light-scattering chromatogram was separated, dried, redissolved in aqueous solution and run through the analytical GPC system. The cutoff molecular weight M^* corresponding to the largest cluster in the polyurethane³⁷ was measured to be 10.62×10^6 (polydispersity 1.10). The dynamic light scattering results obtained by the cumulants analysis on samples of different concentrations in deionized water are shown in Figure 4. It can be seen that at concentrations below 10^{-3} g/g hydrodynamic radii of the particles are consistently lower at 45° than at 15°C, whereas as the concentration increases the clusters at 45°C become larger. This kind of behaviour can be explained by the predominant segment–segment PPO interactions within a given gel cluster at low concentrations, and interparticle interactions

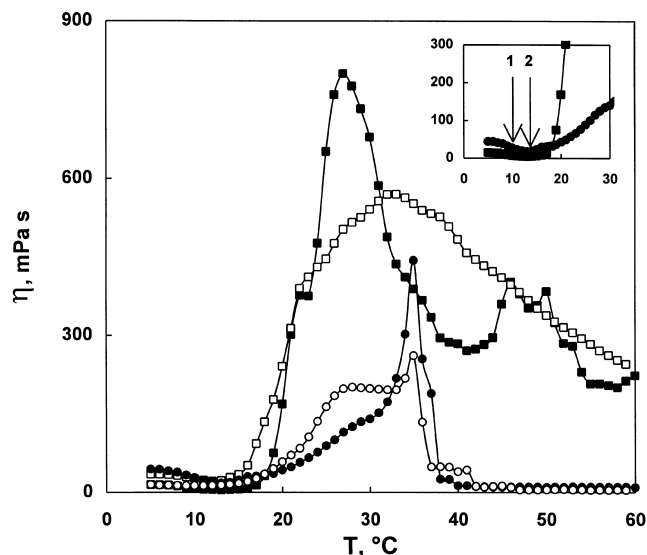


Figure 6 Effect of temperature on the viscosity of a solution of Pluronic L122 (squares) and polyurethane (circles) [$\rho = 1.3$, average mean size of the particles $0.5 \mu\text{m}$]. Filled and open points represent heating and cooling, respectively. The lower critical solution temperatures (LCST) of Pluronic L122 and polyurethane are shown in the insert by arrows 1 and 2, respectively. The effective polymer concentration is 25 wt%, average mean size of the polyurethane particles $0.5 \mu\text{m}$, time of equilibration at each temperature 5 min, shear rate 40 s^{-1}

leading to aggregation when a certain concentration threshold is exceeded. Qualitatively analogous phenomena were observed with uncross-linked Pluronics^{18,58} and polystyrene latexes coated with poly(N-isopropylacrylamide)³⁶.

Temperature-dependent properties of the obtained polyurethane fraction were further studied at high concentration by ^1H and ^{13}C n.m.r., and compared to 10 wt% solution of the parent Pluronic L122 (Figure 5). The line broadening of methyl protons was observed above 10°C in the ^1H n.m.r. of the Pluronic (Figure 5A), in good agreement with the reported cloud point temperature (13°C at 10 wt%⁵⁹). The phenomenon of the entropy-driven aggregation at increasing temperature should be responsible for the restricted motion of the PPO segments in the aggregates, expressing itself in the increasing $\Delta H_{1/2}$. A slight shift of the $\Delta H_{1/2}$ increase to higher temperatures was observed for the polyurethane, when compared to the Pluronic solution, which may be explained by the increasing stiffness of the polyether segments by the end-linking. The increase of stiffness should lead to an increase in temperature of aggregation. These observations agree well with the ^{13}C n.m.r. data (Figure 5B). Indeed, with the increase in temperature, the methyl resonances in PPO segments of either Pluronic or polyurethane broadened and shifted from 17.8 ppm at 8°C to 21.5 ppm at 45°C. The CS versus temperature plot shows a significant percent of the down-field shift above 10°C caused by steric effects due to crowding of the methyls in the formed aggregates.

The proposed formation of aggregates can be correlated with the temperature dependence of the viscosity of the polyurethane suspension (Figure 6). A sharp increase in the viscosity of the Pluronic solution from 10 to 28°C can be explained by the formation of a network of aggregates which was broken by the shear flow. It is interesting to observe that 25 wt% suspension of the polyurethane ($\rho = 1.3$) exhibited a very pronounced viscosification upon heating, although with a two–three-fold smaller maximum

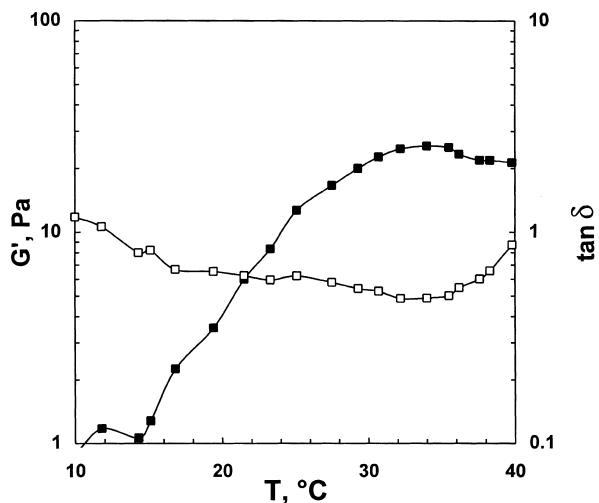


Figure 7 Effect of temperature on storage modulus (G' , filled points) and mechanical loss tangent of 25 wt% suspension of polyurethane ($\rho = 1.3$, average mean size of the particles 0.5 mm) [open points]

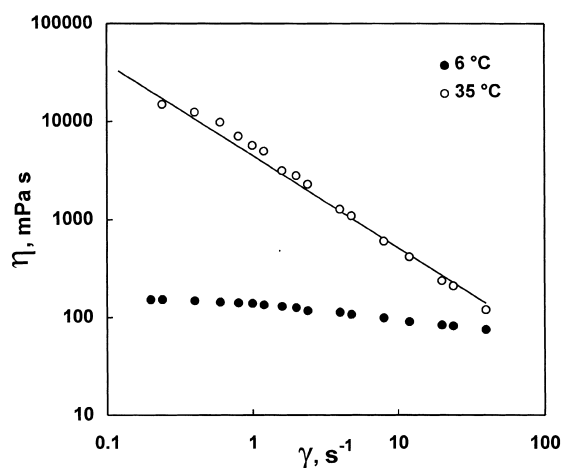


Figure 8 Shear rate dependence of viscosity of 25 wt% suspension of polyurethane ($\rho = 1.5$, average mean size of the particles 0.5 μm) at different temperatures. The solid line is computed by $\eta = \text{const} \times \dot{\gamma}^{q-1}$, where $q = 0.06$

viscosity, when compared with the 25 wt% solution of the parent Pluronic. Higher temperatures required for viscosification of polyurethane than Pluronic (Figure 6) may be related to higher aggregation temperatures, observed by n.m.r. (Figure 5). The insert in Figure 6 shows that the LCST for the polyurethane was about 4°C higher than for the parent Pluronic. Interestingly, the onset of the viscosity increase for the polyurethane coincided with the LCST, whereas gelation of the Pluronic started at about 8°C higher than the corresponding LCST.

The values of storage modulus (G') of the 25 wt% suspension of the polyurethane ($\rho = 1.3$) increased within the temperature range of 10–35°C, indicating the appearance of the viscoelastic network due to temperature-induced cross-links which ‘melted’ somewhat at higher temperatures (Figure 7). The latter process coincided with the increase of the mechanical loss tangent ($\tan \delta$) that showed liquefying^{28,54} of the gel above 35°C.

The shear thinning effect of the 25% suspension of the polyurethane ($\rho = 1.3$) is depicted in Figure 8. At low temperatures, the polyurethane suspension displays almost Newtonian behaviour, whereas when gelled at 35°C

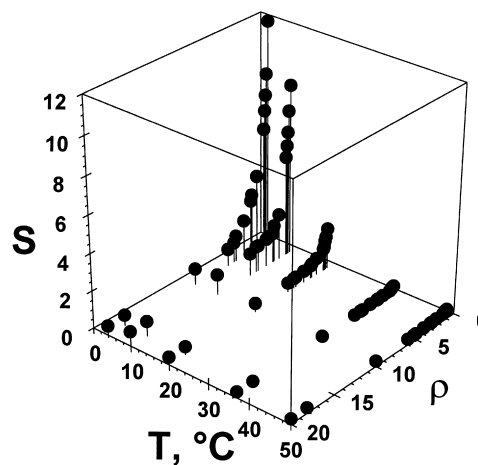


Figure 9 Effect of temperature on swelling degree (S) of polyurethane gels with various cross-linking densities, represented by ρ

(compare with the maximum η in Figure 6) the system is extremely shear thinning. Fitting the data to the power-law model⁶⁰

$$\eta = \text{const} \dot{\gamma}^{q-1}$$

yields $q = 0.06$, which is a very low power-law index characteristic for aqueous latexes and gels⁶¹.

Aggregation phenomena within the particles of cross-linked polyurethane ($\rho \geq 0.8$) are reflected in their swelling behaviour (Figure 9). A decrease of the equilibrium swelling degree (S) with temperature was observed, and was especially pronounced with lightly cross-linked gels. Microscopic experiments showed darkening of the particles with increased temperature, indicating the appearance of dense interparticle domains, which is consistent with the observed agglomeration of PPO segments within the polyurethane network.

The formation of physical networks due to interactions between hydrophobic segments incorporated into domains belonging to different gel clusters may appear to be a rather general phenomenon, since it is found with Pluronic-based particles herein and with other copolymers where one of the blocks consists of units with well-defined LCST, e.g. *N*-isopropylacrylamide⁶².

CONCLUSIONS

Temperature-sensitive polyurethanes were obtained by reacting tris(6-isocyanatohexyl) isocyanurate (TIHI) with polyoxyethylene-*b*-polyoxypropylene-*b*-polyoxyethylene (Pluronic L122). The effect of the initial ratio of equivalents of isocyanate and hydroxyl groups ($\rho = [\text{NCO}]/[\text{OH}]$) set for the synthesis on the polyurethane structure was characterized by light scattering and gel-permeation chromatography. Dependency of the mean weight-average molar mass (M_w) obtained within the range $0.500 < \rho < 0.718$ of the distance (ϵ) to the gel point ($\epsilon = \frac{\rho - \rho_{\text{gel}}}{\rho_{\text{gel}}}$; $\rho_{\text{gel}} = 0.718$ is the critical ratio corresponding to the gelation threshold) showed a scaling parameter corresponding to that predicted by the percolation theory. The dynamic light scattering showed that at concentrations below 10^{-3} g/g hydrodynamic radii of the polyurethane particles are consistently lower at 45 than 15°C, whereas as the concentration increases the clusters at 45°C become larger. This behaviour is explained by the predominant segment–segment PPO interactions within a given gel

cluster at low concentrations and interparticle interactions leading to aggregation above a certain concentration threshold. The temperature-dependent interactions among PPO segments were further confirmed by n.m.r. The formation of physical networks in polyurethane suspensions with temperature increase was followed by a sharp increase in viscosity. The resulting gels appeared to be temperature- and shear-thinning.

ACKNOWLEDGEMENTS

The author is grateful to Prof. Toyochi Tanaka, Prof. Alexander Yu. Grosberg and Dr Michal Orkisz for helpful discussions.

REFERENCES

- Zhou, G., Chen, X. and Smid, J., in *Hydrophilic Polymers. Performance with Environmental Acceptability*, Chapter 2, ed. J. E. Glass, Advances in Chemistry 248, American Chemical Society, Washington, DC, 1996.
- Kanaoka, S., Sawamoto, M. and Higashimura, T., *Macromolecules*, 1991, **24**, 574.
- Brown, R. G. and Glass, J. E., *Proc. Polym. Mater. Sci. Engng*, 1987, **57**, 709.
- Saunders, R. S., Cohen, R. E., Wong, S. J. and Schrock, R. R., *Macromolecules*, 1992, **25**, 2055.
- Zhou, G. B. and Smid, J., *Polymer*, 1993, **35**, 5128.
- Zhou, G. B. and Smid, J., *Langmuir*, 1993, **9**, 2907.
- Zhou, G., Chen, X. and Smid, J., *Proc. Polym. Mater. Sci. Engng*, 1993, **69**, 102.
- Tarng, M.-R., Kaszarski, J. P., Lundberg, D. J., Glass, J. E., in *Hydrophilic Polymers. Performance with Environmental Acceptability*, Chapter 17, ed. J. E. Glass, Advances in Chemistry 248, American Chemical Society, Washington, DC, 1996.
- Amis, E. J., Hu, N., Seery, T. A. P., Hogen-Esch, T. E., Yassini, Hwang, F., in *Hydrophilic Polymers. Performance with Environmental Acceptability*, Chapter 16, ed. J. E. Glass, Advances in Chemistry 248, American Chemical Society, Washington, DC, 1996.
- Tanaka, F. and Edwards, S. F., *J. Non-Newtonian Fluid Mech.*, 1992, **43**, 247.
- Annable, T., Buscall, R., Ettelaie, R. and Whittlestone, D., *J. Rheol.*, 1993, **32**, 695.
- Zhang, Y.-X., Da, A.-H., Butler, G. B. and Hogen-Esch, T. E., *J. Polym. Sci., Polym. Chem.*, 1992, **30**, 1383.
- Wanka, G., Hoffmann, H. and Ulbricht, W., *Colloid Polym. Sci.*, 1990, **268**, 101.
- Almgren, M., Stam, J. V., Lindblad, C., Li, P., Stilbs, P. and Bahadur, P., *J. Phys. Chem.*, 1991, **95**, 5677.
- Kjellander, R. and Florin, E., *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2053.
- Malcom, G. N. and Rowlinson, J. S., *Trans. Faraday Soc.*, 1957, **53**, 921.
- Polyethers*, Part 1, ed. N. G. Gaylord. Interscience, New York, 1963.
- Brown, W., Schillen, K., Almgren, M., Hvidt, S. and Bahadur, P., *J. Phys. Chem.*, 1991, **95**, 1850.
- Alexandridis, P. and Hatton, T. A., *Colloid Surface A*, 1995, **96**, 1.
- Chu, B. and Zhou, Z., *Surfactant Sci. Ser.*, 1996, **60**, 67.
- Alexandridis, P., *Curr. Opin. Colloid Interface Sci.*, 1996, **1**, 490.
- Al-Saden, A. A. R., Florence, A. T. and Whateley, T. L., *Int. J. Pharm.*, 1980, **5**, 317.
- Al-Saden, A. A. R., Florence, A. T. and Whateley, T. L., *Colloids Surf.*, 1981, **2**, 49.
- Law, T. K., Whateley, T. L. and Florence, A. T., *Int. J. Pharm.*, 1984, **21**, 277.
- Ping, Q., Law, T. K., Whateley, T. L. and Florence, A. T., *Int. J. Pharm.*, 1990, **61**, 79.
- Topchieva, I. N., Momot, I. G., Ivanova, V. P. and Efremova, N. V., *Moscow Univ. Chem. Bull.*, 1990, **45**, 95.
- Yekta, A., Nivaggioli, T., Kanagalingam, S., Xu, B., Masoumi, Z. and Winnik, M.A., in *Hydrophilic Polymers. Performance with Environmental Acceptability*, Chapter 19, ed. J. E. Glass, Advances in Chemistry 248, American Chemical Society, Washington, DC, 1996.
- Winter, H. H. and Mours, M., *Adv. Polym. Sci.*, 1997, **134**, 165.
- Kingston, B. H., Gary, J. J. and Hellwig, W. B., *Anal. Chem.*, 1969, **41**, 86.
- Graham, N. B., Nwachuki, N. E. and Walsh, D. J., *Polymer*, 1982, **23**, 1345.
- Bromberg, L., *J. Appl. Polym. Sci.*, 1996, **59**, 459.
- Kajiwarra, K., Burchard, W., Kowalski, M., Neger, D., Dušek, K., Matejka, L. and Tuzar, Z., *Makromol. Chem.*, 1984, **185**, 2543.
- Adam, M., Delsanti, M., Munch, J. P. and Durand, D., *J. Physique*, 1987, **48**, 1809.
- Koppel, D. E., *J. Chem. Phys.*, 1972, **57**, 4814.
- Brown, J. C., Pusey, P. N. and Dietz, R., *J. Chem. Phys.*, 1975, **62**, 1136.
- Zhu, P. W. and Napper, D. H., *Langmuir*, 1996, **12**, 5992.
- Schosseler, F., Benoit, H., Grubisic-Gallot, Z., Strazielle, Cl. and Leibler, L., *Macromolecules*, 1989, **22**, 400.
- Rassing, J., McKenna, W. P., Bandyopadhyay, S. and Eyring, E. M., *J. Molec. Liquids*, 1984, **27**, 165.
- Gronski, W., *Makromol. Chem.*, 1991, **192**, 591.
- Deguchi, S., Akiyoshi, K. and Sunamoto, J., *Macromol. Rapid Commun.*, 1994, **15**, 705.
- Chen, G. and Hoffman, A. S., *Nature*, 1995, **373**, 49.
- Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J. and Smith, P., *Polym. J.*, 1985, **17**, 117.
- Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J. and Smith, P., *Macromolecules*, 1986, **19**, 2466.
- Wilson, L. R. and Tomalia, D. A., *Polym. Prepr.*, 1989, **30**, 115.
- Ilavský, M. and Dušek, K., *Polymer*, 1983, **24**, 981.
- Flory, P. J., *J. Am. Chem. Soc.*, 1941, **63**, 3083.
- Stockmayer, W. H., *J. Chem. Phys.*, 1945, **11**, 45.
- Kaczarski, J. P. and Glass, J. E., *Macromolecules*, 1993, **26**, 5149.
- Manaresi, P. and Munari, A., in *Comprehensive Polymer Science*, Vol. 5, Chapter 23, ed. G. Allen. Pergamon Press, Oxford, 1989.
- Stauffer, D., Coniglio, A. and Adam, M., *Adv. Polym. Sci.*, 1982, **44**, 103.
- Stauffer, D., in *On Growth and Forms*, eds H. E. Stanley and N. Ostrowsky. Martinus Nijhoff, Amsterdam, 1986.
- Stauffer, D., *Introduction to Percolation Theory*. Taylor and Francis, London, 1985.
- Adam, M. and Lairez, D., in *Physical Properties of Polymeric Gels*, ed. J. P. Cohen Addad. John Wiley, New York, 1996, pp. 87–142.
- te Nijenhuis, K., *Adv. Polym. Sci.*, 1997, **130**, 1.
- Cooper, A. R., in *Polymers: Polymer Characterization and Analysis*, ed. J. I. Kroschwitz. John Wiley, New York, 1990, p.481.
- Hester, R. D. and Mitchell, P. H., *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18**, 1727.
- Aharoni, S. M., Crosby, C. R. and Walsh, E. K., *Macromolecules*, 1982, **15**, 1093.
- Zhou, Z. and Chu, B., *Macromolecules*, 1994, **27**, 2025.
- BASF Performance Chemicals. Pluronic® and Tetronic® Surfactants*. BASF, Mount Olive, NJ, 1996.
- Cross, M. M., *J. Colloid Sci.*, 1965, **20**, 417.
- Quemada, D., *Rheol. Acta*, 1978, **17**, 643.
- Bromberg, L., *J. Phys. Chem. B*, 1997, **101**, 504.