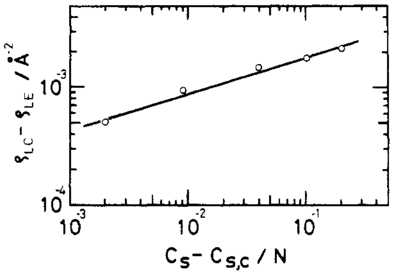

Figure 8. Double logarithmic plot of the density gap ($\rho_{LC} - \rho_{LE}$) between the liquid-condensed and liquid-expanded regions vs. the difference in KBr concentration ($C_s - C_{s,c}$) from 0.001 N.

as $\epsilon = -A(\partial\pi/\partial A)$ was performed by a polynomial fit, but there was considerable scatter in the calculated ϵ. Thus we could not determine the exponent by fitting the compressibility ϵ to power laws of the difference in KBr concentration from the critical concentration of KBr.

Conclusions

Poly(4-vinylpyridines) were fully quaternized with three *n*-alkyl bromides by the spontaneous polymerization of 4-vinylpyridine. At the air–water interface each poly(vinylpyridinium) salt attached with *n*-alkyl chain makes an insoluble and stable monolayer and shows a distinct flat portion, indicating a first-order transition for a liquid-expanded to liquid-condensed phase transition. The range of the flat portion in the π–A isotherms shifts with higher surface pressure and becomes narrower with decreasing KBr concentration. The origin of the force that governs a first-order transition is contributed by the small cooperative cohesive energy, i.e., cohesive surface pressure. This fact was confirmed by the measurement of the interfacial pressure of the polyelectrolyte monolayer at the oil–water interface.

Registry No. PVP·$H_3C(CH_2)_5Br$, 60595-47-3; PVP·$H_3C(CH_2)_7Br$, 76010-13-4; PVP·$H_3C(CH_2)_{11}Br$, 59950-03-7; KBr, 7758-02-3.

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Liquid-Expanded to Liquid-Condensed Phase Transition in Polyelectrolyte Monolayers on the Aqueous KBr Solution. 2. Temperature Dependence

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ABSTRACT: Surface pressure (π)–surface area (A) (π–A) isotherms have been obtained for a series of monolayers of poly(4-vinylpyridinium bromides) that were fully quaternized by three different *n*-alkyl chains (n = 6, 8, and 12) at the air–aqueous KBr solution interface as a function of temperature. In the π–A isotherm the flat portion corresponding to the so-called liquid-expanded to liquid-condensed transition, being simply a first-order transition, was observed even if the temperature changed. π–A isotherms condense with decreasing temperature. At higher KBr concentration a variation of the surface pressure with temperature was observed for the transition from liquid condensed to a solidlike film, whereas at lower KBr concentration a temperature dependence was also observed for the transitions from liquid expanded to liquid condensed as well as liquid condensed to solidlike film. The heats and entropies associated with the transition from liquid-condensed to liquid-expanded film were evaluated by applying the two-dimensional Clausius–Clapeyron equation. The values of these thermodynamic quantities were smaller than the previous data for lipid and polymer monolayers and decreased with decreasing temperature. The transition from liquid-expanded to liquid-condensed film was not easily interpreted in terms of the crystallization of the *n*-alkyl chain attached to poly(4-vinylpyridine) but was contributed by the freedom in the motion of the pyridinium ring adsorbed on the water surface.

A polyelectrolyte that gives an insoluble and stable polyelectrolyte monolayer spread at the air–water interface usually should contain two important characteristics: (1) a hydrophobic character, which is insoluble in the water subphase and makes a stable monolayer and (2) a hydrophilic character originating from charged group of the polyelectrolyte, which anchors the polyion to the water surface. Thus, an amphiphilic character will determine the surface pressure of polyelectrolyte monolayers.

Hydrophobicity related to cohesion due to the hydrocarbon components in the polyelectrolyte will be easily changed by varying thermodynamic parameters such as temperature, while electrical interaction such as an electrostatic force between charged groups strongly depends on salt concentration and the salt species in the water subphase.

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For studies[2,3] of uncharged polymer monolayers spread at the air-water interface, some interesting conclusions concerning the coherence of the monolayers and their interactions with the water subphase were obtained from the variation of the surface pressure with temperature. Particularly, the measurement of surface pressure as a function of temperature is useful to evaluate the heats and entropies for polymer chains in two-dimensional space. However, systematic studies about polyelectrolyte monolayers are lacking compared with uncharged polymer monolayers.

In a previous paper[4] we investigated the influence of salt in the water subphase on the surface pressure of fully quaternized poly(4-vinylpyridines) (PVP) monolayers with *n*-hexyl, *n*-octyl, and *n*-dodecyl bromides. The surface pressure (π)–surface area (A) (π–A) isotherms strongly depend on the KBr concentration and the length of *n*-alkyl chain attached to PVP. For some KBr concentration ranges the flat portion in π–A isotherms corresponding to the so-called phase transition from liquid-expanded (LE) to liquid-condensed (LC) film was observed to indicate a first-order transition. The limiting area is independent of *n*-alkyl chain and KBr concentration and shows that at the highly compressed state the quaternized PVP chains adsorb with the pyridinium ring lying flat and the *n*-alkyl chain protruding out of water surface. This means that the quaternized PVP behaves as a comb-shaped polymer in the compressed state. Therefore, by measurement of the temperature variation of surface pressure, it is expected that the contribution of cohesion between *n*-alkyl chains to the transition in the π–A isotherm can be verified in comparison with the KBr concentration dependence of surface pressure.

The aim of this paper is to measure the surface pressure of the fully quaternized PVP monolayers attached with three different *n*-alkyl bromides as a function of temperature to clarify the nature of the transition. The characteristics of their π–A isotherms will be discussed about the phase changes of LE to LC film in two-dimensional space based on some thermodynamical quantities such as heats and entropies associated with the transition.

Experimental Section

Materials. Quaternized poly(4-vinylpyridines) (PVP) are prepared by the spontaneous polymerization[5] of freshly distilled 4-vinylpyridine with accompanied quaternization by *n*-alkyl bromides (n = 6, 8, and 12) in distilled dimethylcellosolve at around −15 °C as described previously.[4] The resulting quaternized polymers were washed several times with a large amount of dimethylcellosolve, and, then, the polymers separated by filtration were dissolved in methanol and precipitated into excess distilled water. An additional dissolution (in methanol) and precipitation (in water) sequence was repeated to purify the polymers. Precipitants were dried under vacuum to remove water at room temperature.

The characterization of the polymers was performed by elemental analysis and Knauer vapor pressure osmometry in methanol at 30 °C to determine molecular weight.

Deionized water was supplyed from a Millipore Q-TM system. Spectral grade methanol was used as a spreading solvent without further purification. Analytical quality KBr was used without further purification.

Method. The surface pressure of the quaternized PVP monolayer spread at the air–aqueous KBr solution interface has been measured by the Wilhelmy plate method with a glass plate or a platinum plate attached to a force transducer (Sinko Denki Co. Type 1301) fed into a home-built phase-sensitive amplifier. The sensitivity in detecting surface pressure changes was 0.03 dyn/cm.

Spreading of the monolayers on the surface of aqueous KBr solution containing in a Teflon trough (size 10 × 900 × 160 mm)[6] was carried out be delivering the methanol solution from a Terumo microsyringe, and 30 min was allowed for evaporation of the methanol. The surface concentration of the monolayers was changed by successive compression.

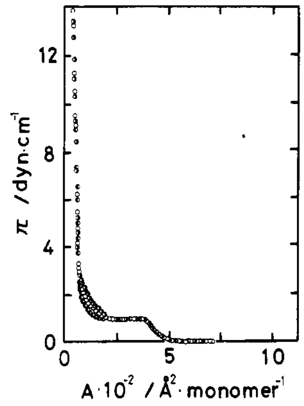

Figure 1. π–A isotherms of the PVPC6 monolayer at the air–aqueous 0.2 N KBr solution interface as a function of temperature: (◑) 35 °C; (○) 25 °C; (◐) 15 °C.

The temperature of the aqueous KBr solution subphase in the trough was controlled at the measuring temperature by circulating thermostated water through a glass coil placed in the bottom of the trough. The error of the controlled temperature is ±0.1 °C.

Results and Discussion

Figure 1 shows π–A isotherms of poly(4-vinyl-*N*-*n*-hexylpyridinium bromide) (PVPC6) monolayer spread at the air–0.2 N aqueous KBr solution interface as a function of temperature. We can notice some features from the figure. These π–A isotherms include the flat portion corresponding to the LE–LC transition, which is simply a first-order transition. Up to the flat portion they superimpose independent of temperature within experimental error. Beyond the transition region the surface pressure at the same surface area increases with increasing temperature until the π–A isotherms again nearly coincide and attain a solidlike monolayer around π = 4 dyn/cm, where the freedom of motion of the pyridinium ring is restricted. Thus, the temperature variation of the π–A isotherm is observed for changes from liquid-condensed to solid states of the monolayer. Careful inspection of data above π = 4 dyn/cm shows that the surface pressure at constant surface area becomes a little larger with increasing temperature. However, the limiting area extrapolated the straight portion of the π–A isotherm to π = 0 is obtained at 48 ± 1 Å^2/(monomer unit) independent of temperature. This area is in agreement with the area of a conformation with the pyridinium ring adsorbed lying flat on the water surface and the *n*-alkyl chain protruding out of the water surface.

Figure 2 presents π–A isotherms of a PVPC6 monolayer spread at the air–0.1 N aqueous KBr solution interface for three different temperatures. The characteristic behavior of the π–A isotherms is quite similar to that for the 0.2 N aqueous KBr solution. The surface pressure at the flat portion and the surface areas of beginning and ending points of the LE–LC transition region are listed in Table I. The data at constant KBr concentration are in good agreement with each other independent of temperature.

For a relatively low salt concentration in the water subphase the temperature dependence of the π–A isotherm shows a different behavior from that for higher salt concentrations. As shown in Figure 3 for the π–A isotherms of a PVPC6 monolayer spread at the air–0.01 N aqueous KBr solution interface, a temperature variation is observed above the surface area where the flat portion in π–A isotherm begins. The surface pressure at constant surface area increases and the range of the flat portion becomes narrower with increasing temperature. This temperature

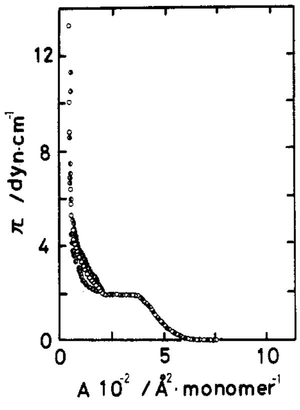

Figure 2. π–A isotherms of the PVPC6 monolayer at the air–aqueous 0.1 N KBr solution interface as a function of temperature: Symbols are the same as in Figure 1.

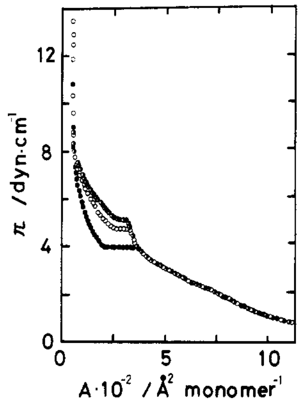

Figure 3. π–A isotherms of the PVPC6 monolayer at the air–aqueous 0.01 N KBr solution interface as a function of temperature: (●) 5 °C. Other symbols are the same as in Figure 1.

Table I
Temperature Dependence of the Equilibrium Surface Pressure π_t and Surface Areas A_{LE} and A_{LC} of the Beginning and Ending Points of the Flat Portion in the π-A Isotherm for a PVPC6 Monolayer at the Air-Aqueous KBr Solution Interface

temp, °C	π_t, dyn/cm	A_{LE}, Å^2/(monomer unit)	A_{LC}, Å^2/(monomer unit)
	KBr Concentration: 0.2 N		
35	0.92	393	204
25	0.91	403	218
15	0.92	395	197
	KBr Concentration: 0.1 N		
35	1.94	376	219
25	1.92	374	225
15	1.93	376	227

dependence appears similar to salt concentration dependency:[4] with decreasing salt concentration in the water subphase the surface pressure increases and the flat portion range becomes narrower. Beyond the flat portion the temperature dependence of the surface pressure is the same as in Figures 1 and 2.

However, below the flat portion the surface pressure becomes independent of temperature. This leads us to conclude that the electrostatic repulsive force mainly determines the surface pressure because there is no variation of surface pressure with salt species or different interfaces such as the air–water and the oil–water as described previously.[4]

A similar temperature dependence of surface pressure was observed for a PVPC6 monolayer spread at the air–0.003 N aqueous KBr solution interface and for poly(4-vinyl-N-n-octnylpyridinium bromide) (PVPC8) and poly(4-vinyl-N-n-dodecylpyridinium bromide) (PVPC12) monolayers spread at the air–0.01 N aqueous KBr solution interface as shown in Figures 4–6, respectively.

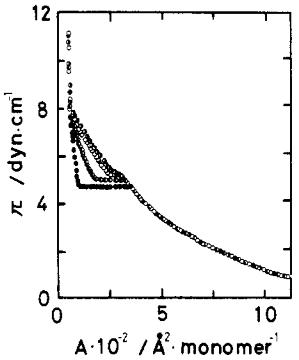

Figure 4. π–A isotherms of the PVPC6 monolayer at the air–aqueous 0.003 N KBr solution interface as a function of temperature. Symbols are the same as in Figures 1 and 3.

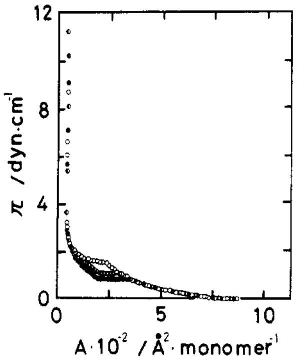

Figure 5. π–A isotherms of the PVPC8 monolayer at the air–aqueous 0.01 N KBr solution interface as a function of temperature. Symbols are the same as in Figure 4.

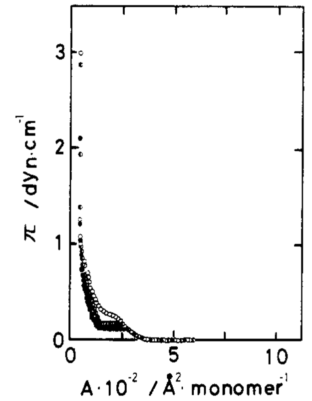

Figure 6. π–A isotherms of the PVPC12 monolayer at the air–aqueous 0.01 N KBr solution interface as a function of temperature. Symbols are the same as in Figure 4.

From Figures 3–6 are observed the flat portions in the π–A isotherms, even for changing temperature, at a relatively low KBr concentration in the water subphase. Since we can regard the flat portion in the π–A isotherm, corresponding to the LE–LC transition, as a first-order transition, we evaluate the heats ΔH and entropy ΔS of the LE–LC transition of a polyelectrolyte monolayer by applying the two-dimensional Clausius-Clapeyron equation

$$\frac{\partial \pi_t}{\partial T} = \frac{\Delta H}{T(A_{LC} - A_{LE})} = \frac{\Delta S}{(A_{LC} - A_{LE})} \quad (1)$$

In this equation T is the absolute temperature, π_t is the surface pressure at the flat portion in the π–A isotherms, and A_{LE} and A_{LC} are the surface areas of the beginning and

Table II
Equilibrium Surface Pressure π_t, Surface Areas A_{LE} and A_{LC} of Beginning and Ending Points of the Flat Portion in the π–A Isotherms, and Heats ΔH and Entropies ΔS of the Transition for the Fully Quaternized PVP Monolayers at the Air-Aqueous KBr Solution Interfaces

temp, °C	π_t, dyn/cm	A_{LE}, Å^2/(monomer unit)	A_{LC}, Å^2/(monomer unit)	$\Delta H \times 10^{14}$, erg/(monomer unit)	$\Delta S \times 10^{16}$, erg/(monomer unit·deg)
			PVAC6 (0.003 N)		
35	5.28[a]				
25	5.09	307	267	−2.55	−0.86
15	4.96	323	182	−8.48	−2.95
5	4.68	342	109	−13.65	−4.91
			PVPC6 (0.01 N)		
35	5.11	305	269	−4.41	−1.43
25	4.72	324	249	−8.92	−2.99
5	3.93	397	182	−23.80	−8.56
			PVPC8 (0.01 N)		
25	1.38[a]				
15	1.05	336	237	−8.55	−2.97
5	0.81	395	223	−14.30	−5.14
			PVPC12 (0.01 N)		
25	0.23[a]				
15	0.18	327	213	−2.04	−0.71
5	0.11	349	180	−2.89	−1.04

[a] The surface pressure corresponds to the kink point in the π–A isotherm.

ending points of the flat portion, respectively.

Since the LE–LC transition was usually observed as a kink point corresponding to a single slope change (likely a second-order transition) in the π–A isotherm,[7] some attempts[8] to estimate the difference in the surface areas between the LE and LC states have been performed to evaluate the heats of the transition. If the LE–LC transition is not proceeding under constant pressure, i.e., there is a kink instead of a flat portion in the π–A isotherm, the heats of transition evaluated in terms of the two-dimensional Clausius-Clapeyron equation includes a work term. However, the contribution of the work term to the evaluated ΔH is not very much. For example, for a phospholipid monolayer such as dipalmitoyllecithin,[9] a work term amounts to about 1 kcal/mol, while ΔH is over 10 kcal/mol.

For the quaternized PVP series, however, the contribution of a work term to ΔH is zero because the LE–LC transition occurs at constant pressure. The data for π_t, A_{LE}, and A_{LC} are summarized in Table II as a function of measuring temperature, together with the surface pressure at the kink point. A linear plot of π_t against measuring temperature shows a nearly straight line within experimental errors and gives $d\pi_t/dT = 0.04$, 0.03, and 0.0062 dyn·cm^{-1}·deg^{-1} for PVAC6, PVAC8, and PVAC12 monolayers spread at the air–0.01 N KBr aqueous solution interface, respectively. The value of $d\pi_t/dT = 0.02$ dyn·cm^{-1}·deg^{-1} is obtained for the PVAC6 monolayer spread at the air–0.003 N KBr aqueous solution interface. The positive value of $d\pi_t/dT$ shows that the quaternized PVP monolayers condense with decreasing temperature. The absolute value of $d\pi_t/dT$ is much smaller than $d\pi_t/dT \sim 1.0$ dyn·cm^{-1}·deg^{-1} for fatty acid[10] and phospholipid[9,11] monolayers, but its order of magnitude is the same as nonionic polymer monolayers,[3] which also have a phase transition showing a break in the slope of the π–A isotherm. Therefore, for the lipid and nonionic polymer monolayers the π_t value was taken as the surface pressure at the kink point in the π–A isotherm.[3,9–11]

Our experimental data on values of $d\pi_t/dT$ that are smaller than those of uncharged polymer monolayers are in agreement with the experimental results of phospholipid monolayers observed by Albrecht, Gruler, and Sackmann.[11] They measured the surface pressure of charged (α-dimyristoylphosphatidic acid) and uncharged (α-dipalmitoyllecithin) monolayers as a function of temperature. They obtained a smaller temperature dependence of surface pressure at the transition of the charged phospholipid monolayer than that of the uncharged phospholipid monolayer.

The heats ΔH evaluated from eq 1 are also listed in Table II. These ΔH values can be simply equated to the change in heat content accompanying the transition from an LE to an LC film.

The evaluated ΔH is usually related to the heat of fusion for an n-alkyl chain in lipid monolayers,[8–10] and for this reason an increase of the evaluated heats with increasing n-alkyl chain has been reasonably interpreted. Therefore, it was concluded that the LE–LC transition is caused by the chain crystallization at the air–aqueous solution interface. However, our experimental results show that the evaluated ΔH decreases with increasing n-alkyl chain at constant temperature as shown in Table II. In addition, this trend does not depend on the route of the evaluation of the difference in area between LE and LC states if we take A_{LC} in eq 1 as the limiting area instead of the surface area at the end of the flat portion in the π–A isotherm according to the method of Phillips and Chapman,[9] the absolute value of ΔH becomes larger but its order does not change with n-alkyl chain length because the constant limiting area is independent of the n-alkyl chain length. For the temperature range 15–25 °C the absolute value of evaluated ΔH is smaller than $\Delta H \sim -20 \times 10^{-14}$ erg·molecule^{-1} for uncharged polymer monolayers.[3]

The entropy change ΔS also can be evaluated from eq 1 and the evaluated ΔS values are summarized in Table II. The absolute value of the evaluated ΔS is smaller than that of uncharged polymer monolayers[3] in the temperature range 15–25 °C and also is much smaller than the entropy ($\Delta S \sim -7 \times 10^{-16}$ erg·molecule^{-1}·deg^{-1}) associated by a crystallization of hydrocarbon chains. The smaller negative value of ΔS seems to be contributed by the large freedom in motion of the pyridinium ring adsorbed on the water surface due to the electrostatic force. This is revealed from a comparison of ΔS values of PVPC6 for KBr concentrations of 0.01 and 0.003 N. Therefore, this fact means that the nature of the LE–LC transition is a van der Waals type rather than a fluid to crystal type of transition.

Conclusions

The π–A isotherms of the fully quaternized PVP monolayers spread at the air–aqueous KBr solution interface include the flat portion corresponding to LE–LC transition even with changing temperature. They show a remarkable temperature dependency and condense with decreasing temperature. Application of the two-dimensional Clausius–Clapeyron equation gives heats and entropies associated with the transition that are relatively smaller than those of uncharged polymer monolayers due to the freedom of motion of pyridinium ring adsorbed at the air–aqueous KBr solution interface. Thus, the nature of the LE–LC transition of the quarternized PVP monolayers is not simply related to a fluid to crystal transition.

Registry No. PVPC6, 107455-36-7; PVPC8, 74343-05-8; PVPC12, 75503-70-7; KBr, 7758-02-3.

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Detection of T_{ll} in Styrene–Ethyl Acrylate Random Copolymers by Differential Scanning Calorimetry and Dynamic Mechanical Analysis

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ABSTRACT: There is a paucity of planned experimental investigations concerning the liquid–liquid transition/relaxation (T_{ll}) in random copolymers. A styrene–ethyl acrylate (S/EA) series, containing both homopolymers and seven copolymers of varying composition, has been prepared by free radical methods and studied by both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The T_{ll} and T_g transitions were reliably and reproducibly detected by both methods, varied smoothly as a function of copolymer composition, and obeyed the relationship $T_{ll} = 1.2T_g$. The observed data are discussed within the framework of the Lobanov–Frenkel model for molecular events occurring at T_{ll}.

Introduction

The existence of a discrete molecular transition and/or relaxation occurring in polymers above the glass transition (T_g) was predicted by Ueberreiter in 1943[1] and was formalized and designated as the liquid–liquid transition (T_{ll}) by Boyer in 1963.[2] In 1966 it was postulated that T_{ll} was a general transition associated with the amorphous state of polymers and it was shown that there were already considerable published data (thermal, spectroscopic, and dynamic mechanical) demonstrating this phenomenon in atactic polystyrene.[3] In the ensuing 20 years, studies of T_{ll} have generated an extensive set of experimental observations both supporting and criticizing the T_{ll} phenomenon. Two review articles summarize both the experimental evidence and theoretical arguments on both sides of the controversy.[4,5] It should also be noted that some of the various possible liquid state transitions/relaxations—including T_f (fusion–flow temperature), T_{ll} (an intermolecular process), and $T_{1\rho}$ (an intramolecular process, formerly $T_{ll'}$)—have been compared and contrasted.[5]

The nature of the molecular event(s) occurring at T_{ll} seems to be most consistent with the hypothesis of Frenkel[6,7] that macromolecules in the liquid state above T_g (but below T_{ll}) exhibit both gaslike random coil behavior of the entire macromolecule and liquidlike behavior characterized by segment–segment contacts or interactions (either between chains or within the same chain). As the temperature increases to T_{ll} the attractive forces (primarily enthalpic) are overcome and "segmental melting" occurs. The gain in entropy of the system as the individual chains are freed from segmental restraints provides the driving force for the transition/relaxation. In contrast to many of the published reports, the present study is the first one intentionally designed to investigate the T_{ll} relaxation in random *copolymers* and is directed toward answering four questions:

a. Does the T_{ll} relaxation occur in random copolymers?

b. Can this transition be detected by more than one type of experimental method?

c. Does T_{ll} in such a system vary in a smooth and predictable manner as the copolymer composition is varied?

d. Is there a systematic, well-defined relationship between T_g and T_{ll} in random copolymers?

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