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Evolution of Polyurethane Gel Fraction near the Gelation Threshold

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The gelation process by polycondensation leading to polyurethane gels was studied below and near the gel point. The growth process of clusters was investigated by light scattering[1] and small-angle neutron scattering.[2] Mass distribution and weight-average molecular weight, near the gel point, are found to follow power laws with exponents $\tau = 2.2 \pm 0.04$ (ref 2) and $\gamma = 1.71 \pm 0.06$ (ref 1), respectively. Thus, below the gel point the growth process of branched polymers is described by percolation theory.[3,4]

The experiments reported here are performed beyond the gel point. We are interested in the evolution of the gel fraction as a function of the reaction extent p and as a function of the distance ϵ to the gel point: $\epsilon = p - p_c$, p_c being the reaction extent at the gel point.

Near the gel point, the gel fraction G, which represents the probability that a monomer belongs to the infinite cluster, increases with ϵ following a power law[5]

$$G \sim \epsilon^\beta \qquad (1)$$

The exponent β is related to the exponents τ and γ:

$$\beta = \gamma(\tau - 2)/(3 - \tau) \qquad (2)$$

Percolation theory[5] predicts $\beta = 0.43$ ($\tau = 2.2$, $\gamma = 1.74$) and the classical mean field theory of gelation, introduced by Flory–Stockmayer,[6,7] gives $\beta = 1$ ($\tau = 2.5$, $\gamma = 1$).

Flory and Stockmayer theories lead to similar results only near the gel point. Following Flory's approach[6] G must increase with ϵ as

$$G = 4\epsilon(3 + 4\epsilon^2)/(1 + 2\epsilon)^3 \qquad \text{for} \quad 0 \leqslant \epsilon \leqslant 1 - p_c \qquad (3)$$

Polyurethane samples were prepared without solvent in the presence of catalyst (dibutyltin dilaurate) by condensation of hydroxyl groups belonging to trifunctional units (poly(oxypropylenetriol) with molecular weight of 700) and isocyanate groups belonging to difunctional units (hexamethylene diisocyanate). The stoichiometric ratio, defined as $p = [\mathrm{NCO}]/[\mathrm{OH}]$ where [NCO] and [OH] are the concentrations of NCO and OH groups present initially, is determined by weighing. If $p < 1$, at complete reaction, p is proportional to the number of OH groups which have reacted and is taken as the reaction extent. The verification of the absence of NCO groups at complete reaction has been described in a previous paper.[8]

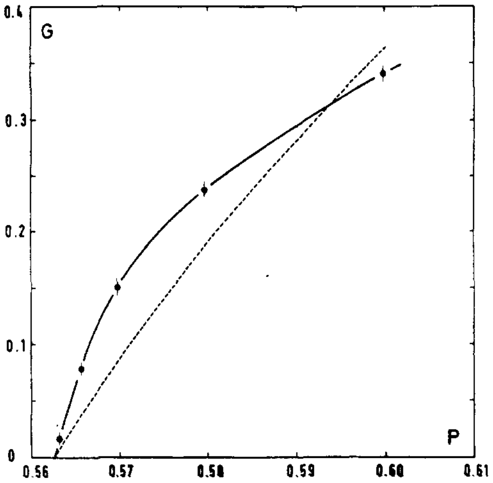

Figure 1. Evolution of the gel fraction G as a function of the extent of reaction p (linear scale). The solid line is a guide for the eye. The dashed line represents the evolution of the gel fraction according to Flory's expression (relation 3 with p_c = 0.5624).

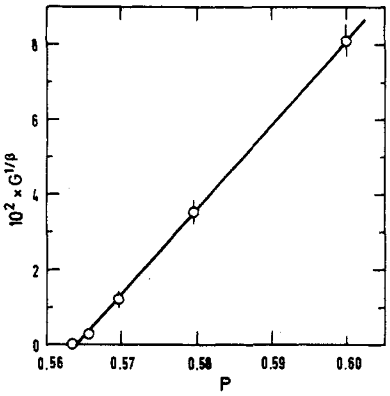

Figure 2. Exponent β (=0.43) determined from τ and γ exponent values measured below the gel point (1) accounts for the gel fraction measured beyond the gel point: $G^{1/\beta}$ is a linear function of the extent of reaction p.

Sol extractions were performed in the following way: a polyurethane sample (≈7 g) was put into a porous capsule, large enough (≈40 cm^3) to allow a complete swelling of the gel. In order to extract the soluble polymers through the porous membrane, the capsule was introduced into a closed container holding 100 cm^3 of good solvent tetrahydrofurane (THF). Then, after 2 days, the solution of extracted polymers in THF was removed, THF was evaporated under reduced pressure at 30 °C, and polymer clusters were weighted. This operation was repeated several times until the weight of total extracted polymers became a constant within about 10^{-3} g. The mass fraction of gel is calculated by difference between the mass of the extracted clusters and the total mass of the sample. The stoichiometric ratio p and the corresponding gel fraction measured are given in Table I.

Table I
Experimental Stoichiometric Ratio p and Mass Fraction of Gel G

p^a	0.5617	0.5632	0.5656	0.5695	0.5796	0.5999
G	0	0.016 ± 0.005	0.078 ± 0.006	0.150 ± 0.007	0.237 ± 0.007	0.339 ± 0.007

[a] The precision on p is 10^{-4}.

Below a critical stoichiometric ratio p_c, samples are a collection of finite clusters which can be completely extracted ($G = 0$). Beyond p_c, samples present a giant cluster which cannot be extracted. The experimental results obtained with samples prepared at the two lower p values (see the table) lead us to locate the p_c value inside the following range: $0.5617 < p_c < 0.5632$. This p_c location is different from the $p_c = 0.5596$ determined by solubility measurements in a similar system.[1] This discrepancy can be explained by the fact that the material used did not come from the same synthesis run.

In the ϵ range investigated ($\epsilon \leqslant 3.8 \times 10^{-2}$), following the mean-field theory the gel fraction G should be a linear function of the reaction extent p, or approximatively linear (see eq 3). This is ruled out by Figure 1 which shows that the evolution of G as a function of p, on a linear scale, presents a strong downward curvature. In Figure 2, $G^{1/\beta}$ is plotted as a function of p where β is the exponent value deduced from the τ and γ values measured below the gel point ($\beta = 0.43 \pm 0.12$). The linear behavior in this representation (Figure 2) indicates that this β value is compatible with the present results but the p_c value determined in this manner $p_c = 0.5639$ is slightly out the p_c range evaluated from direct extraction measurements. This fact can be due to the difficulties encountered in the extraction of finite polymer clusters very near the gel point.

However, these results show clearly that the growth of polyurethane polymer clusters elaborated below and beyond the gel point is described by the percolation theory. But more experiments must be performed, beyond the gel point, in order to determine more precisely the exponent β and the law governing the decrease of the weight-average molecular weight.

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Communications to the Editor

Novel Nitrogen-Containing Heterocyclic Polymers Derived from the Alternating Ethylene-Carbon Monoxide Copolymer

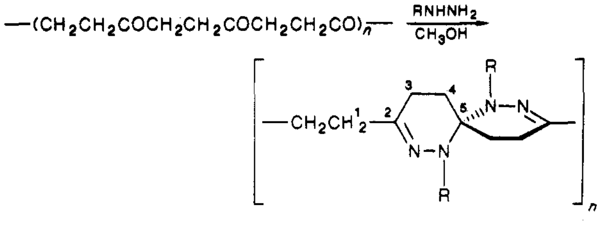
We have recently described a mild, Pd(II)-catalyzed, procedure for the alternating copolymerization of ethylene and carbon monoxide (eq 1).[1] Because of the ease with

$$CH_2{=}CH_2 + CO \xrightarrow[25\ °C]{Pd(PPh_3)_n(MeCN)_{4-n}{}^{2+}} -(CH_2CH_2CO)_n- \qquad (1)$$

which the carbonyl group can be chemically modified, polyketones such as the ethylene—carbon monoxide copolymer (E–CO copolymer) should be excellent precursors for other classes of functionalized polymers. Indeed, about two dozen functionalized polymers incorporating a variety of functional groups have been made starting with the previously reported random E–CO copolymer (C_2H_4:CO > 1).[2] As a precursor polymer, the alternating E–CO copolymer (C_2H_4:CO = 1) has two significant advantages over its random analogue (C_2H_4:CO > 1). First, since carbon monoxide does not homopolymerize, the alternating E–CO copolymer would provide the highest possible concentration of carbonyl groups in the polymer backbone. Second, the 1,4 arrangement of the carbonyl groups in the alternating E–CO copolymer makes additional functionalization procedures possible. Herein, we report the conversion of the alternating E–CO copolymer to two new classes of nitrogen-containing heterocyclic polymers through reactions based on the 1,4 arrangement of carbonyl groups in the backbone.

The addition of hydrazine to a MeOH suspension of the E–CO copolymer at 60 °C caused its complete dissolution to form a new polymer, 1, in near quantitative yield. Following filtration to remove trace impurities, the polymer was isolated by the removal of the solvent. Reprecipitation from CH_2Cl_2–Et_2O yielded an off-white crystalline solid. An analogous reaction of methylhydrazine with the E–CO copolymer produced polymer **2** in near quantitative yield as a crystalline yellow-brown solid.

The structures of both polymers, 1 and **2**, were determined by spectroscopic methods and contained a unique spirofused group (1,2,7,8-tetraazaspiro[5.5]undecane) in the backbone (eq 2). The IR spectrum (Nujol) of polymer 1 exhibited $\bar{\nu}$(N–H) at 3250 cm^{-1}, $\bar{\nu}$(C=N) at 1630 cm^{-1}, and $\bar{\nu}$(C–N) at 1050 cm^{-1}. In its ^{1}H NMR spectrum ($CDCl_3$), three resonances were observed at 2.36, 2.25, and 1.77 ppm with integral ratios of 1:1:1, and these were assigned to the three $-CH_2-$ groups present. The highest field signal was ascribed to the hydrogens on C-4. In addition, the spectrum contained a broad resonance at 6.3–5.8 ppm due to the –NH group. A tiny triplet at 1.06 ppm (J = 7.6 Hz) due to the terminal $-CH_3$ groups of the polymer was also observed. The ^{1}H-coupled ^{13}C NMR spectrum ($CDCl_3$) showed three triplets at 34.1 ppm (J = 129.9 Hz), 28.1 ppm (J = 131.4 Hz), and 22.1 ppm (J = 125.5 Hz) due to the three $-CH_2-$ groups. In addition, singlets were observed at 148.1 and 59.8 ppm and were ascribed to C-2 and C-5, respectively.



(2)

polymer **1**, R = H; polymer **2**, R = CH_3

Polymer 2 showed NMR spectral features analogous to 1 except that the broad resonance at 6.3–5.8 ppm was replaced by a singlet at 2.71 ppm in the ^{1}H NMR spectrum ($CDCl_3$), and a quartet at 36.7 ppm (J = 135.7 Hz) was observed in the ^{1}H-coupled ^{13}C NMR spectrum ($CDCl_3$). These additional resonances were due to the presence of $N{-}CH_3$ group in polymer **2**. In neither polymer was there any evidence for the presence of unreacted carbonyl groups.

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