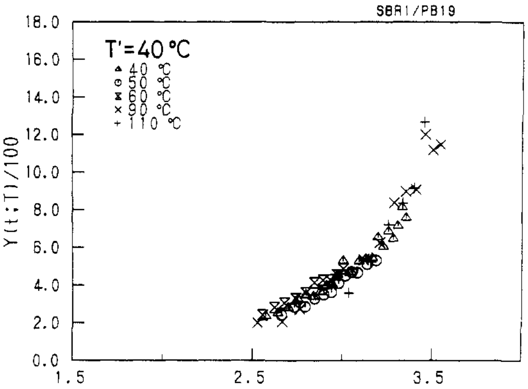

Figure 4. Reduction of Y data at different quench temperatures to a master curve at 40 °C.

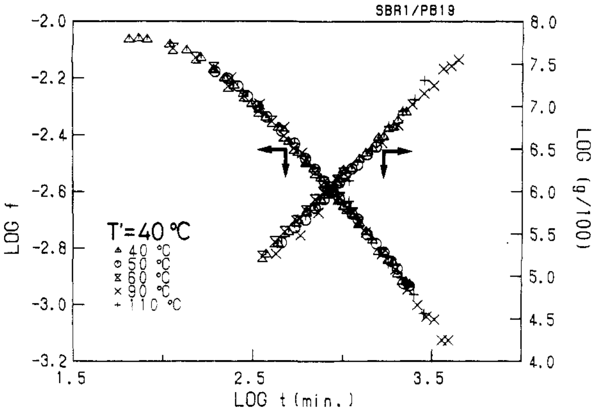

Figure 5. Time changes in f ($\sim \tilde{q}_m$) and g ($\sim \tilde{I}_m$) at 40 °C for a critical SBR1-PB19 blend.

(t/t_c'), where t_c' is the value of $t_c(T)$ at the reference temperature T'; i.e., $t_c' = [\xi_c(T')]^2/D(T')$.

From eq 10 it follows that plots of $Y(t;T)$ against ln t for different T can be reduced to a master curve by horizontal shifting and that multiplication of the master curve $Y(t,T')$ by $t^{3/2}$ gives the values of $(t_c')^{3/2}g(t/t_c')$.

When we find that the data for $X(t;T)$ and $Y(t;T)$ can be reduced to master curves, we can conclude that the system under study obeys the Chou-Goldburg scaling laws. Though incapable of determining the absolute values of f and g, the master curves obtained allow us to see how the exponents α and β in the relations $\tilde{q}_m \sim t^{-\alpha}$ and $\tilde{I}_m \sim t^{\beta}$ vary with time. This information should be important for elucidating the molecular mechanism responsible for the spinodal decomposition of critical binary mixtures.

Application. We made a test of the Chou-Goldburg postulate by applying the above method to the unpublished experimental data of Hashimoto and Takenaka on the critical mixture of a styrene-butadiene rubber 1 (SBR1)/polybutadiene 19 (PB19) blend. (SBR1: $M_w = 1.18 \times 10^5$, $M_w/M_n = 1.18$; styrene content = 20 wt %; trans:cis:vinyl = 0.16:0.23:0.61. PB19: $M_w = 1.90 \times 10^5$, $M_w/M_n = 1.16$; cis:trans:vinyl = 0.19:0.35:0.46.) In so doing, we estimated the necessary values of $D(T)$ by analyzing $I(q,t)$ data for the initial stage of spinodal decomposition in the usual way.[7]

Figures 1 and 2 show the values of $X(t;T)$ and $Y(t;T)$ at five temperatures plotted against log t. These plots can be reduced to master curves by adequate horizontal shifting. Figures 3 and 4 show the results obtained when 40 °C is chosen as the reference temperature T'. Here, the variable t on the abscissa axis refers to the real time scale in the measurement at T'. The amounts of horizontal shifting that were needed for the construction of the master curves are reported by Izumitani et al.[8] in a forthcoming paper. We see that the experimental data of Hashimoto and Takenaka are consistent with the Chou-Goldburg postulate. However, this finding is surprising, because the data are concerned with quench temperatures (40-110 °C) far below T_c of the blend, which was estimated by Izumitani and Hashimoto[9] to be about 400 °C.

The master curves for f and g in Figure 5 have been derived from the data points in Figures 3 and 4. The abscissa variable t again refers to the real time in the measurement at 40 °C. The time scale in which these curves appear is only a little more than one decade. Experimental data covering a wider time scale are needed for checking the range of validity of the Chou-Goldburg postulate. In Figure 5, the master curve for f is distinctly curved, giving α which increases smoothly from about 0.2 to about 0.8 with increasing t. On the other hand, the corresponding curve for g is almost linear, giving β equal to about 2.4. Thus, these results essentially satisfy the relation $\beta = 3\alpha$ in the time scale $t > 370$ min (or log t (min) > 2.4).

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Effect of Increasing Propyl Group Substitution on Permethyl Polyazine

The study of polymers with conjugated π systems that can be oxidatively or reductively doped into a highly conductive state has been of great interest recently.[1] The prototype polymer in this class is polyacetylene,[2] $-(CH{=}CH)_x-$. We have been studying polyazines,[3] $-(N{=}C(R_1)\text{-}C(R_2){=}N)_x-$, that are formally isoelectronic to, but topologically distinct from, polyacetylene. Unlike polyacetylene, polyazines are environmentally stable and so are attractive candidates for useful conducting polymers. Polyazines ($R_1 = R_2 = H$ or $R_1 = R_2 = CH_3$) can be doped to give conducting materials,[3c,3g] but these polymers lack processing characteristics. Organic soluble polyazines are known,[4,5] but these materials do not dope into a highly conductive state.

This report describes the preparation and IR and NMR characterization of long-chain soluble permethyl ($R_1 = R_2 = CH_3$) polyazines with a controlled number of propyl

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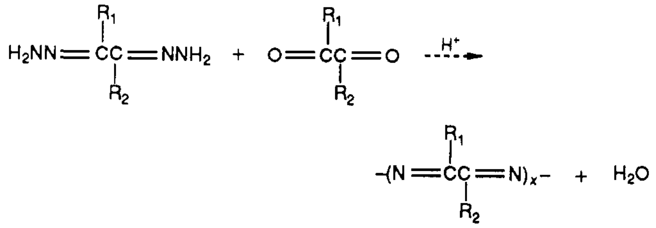
Table I
Synthetic and Analytical Results for $(CH_3C(O))_{2-y}[(C_4H_6N_2)_{1-y}(C_6H_{10}N_2)_y]_x(C(O)CH_2CH_2CH_3)_{2y}$

			elem anal.,[c] %					
y[a]	*x*[b]	% yield	C	H	N	C/N	2 + *y*	decompn temp[d]
1	22	15	66.10 (65.87)	9.25 (9.22)	24.58 (24.49)	3.137	3.000	110–140
0.50	50	93	62.42 (62.39)	8.38 (8.47)	28.55 (28.94)	2.514	2.50	134–178
0.232	50	72	60.86 (61.16)	7.93 (7.88)	31.17 (31.06)	2.296	2.232	214–248
0.127	27	45	59.54 (60.21)	7.64 (8.48)	31.48 (31.22)	2.249	2.127	226–250
0.0605	33	60	58.98 (59.41)	7.50 (7.81)	32.40 (32.63)	2.123	2.0605	232–252
0.0325	9	31	58.56 (58.35)	7.36 (7.50)	30.24 (30.00)	2.268	2.0325	238–254

[a] Found from the mole ratio of diones used in the reaction. [b] Found from the C/N ratio. This method has an upper limit of about 50 monomer units. [c] The experimentally observed elemental analyses are given in parentheses and were found by M–H–W Laboratories, Phoenix, AZ. [d] Measured on a Mel-Temp apparatus and are uncorrected.

groups along the polymer chain. The goal is to prepare materials with the organic solubility afforded by the alkyl side chain, but leading to a conducting material as found in the permethyl derivative.

Polyazines are prepared from the condensation of an α,β-dihydrazone with an α,β-dione under acidic conditions:[6]



By appropriate choice of dihydrazone or dione, or mixtures thereof, the substitution pattern along the polymer chain can be synthetically controlled. Thus for the permethyl polymer, $R_1 = R_2 = CH_3$ for both the dihydrazone and the dione, while for the propyl–methyl polymer $R_1 = CH_2CH_2CH_3$ and $R_2 = CH_3$ for both reactants. In order to regulate the number of propyl groups along the polymer backbone, we used 2,3-butanedione dihydrazone exclusively as the dihydrazone reactant and mixtures of 2,3-butanedione and 2,3-hexanedione as the dione reactant. This gives polymers with composition $-[(C_4H_6N_2)_{1-y}(C_6H_{10}N_2)_y]_x-$, where y is determined by the ratio of 2,3-hexanedione to 2,3-butanedione. The various polymers prepared are given in Table I. As desired, all the polymers prepared, even down to $y = 0.0325$, have some organic solubility, but, not surprisingly, as the percentage of propyl groups decreases, so does the solubility.

The polymer end groups from this synthetic method can be either amino or ketone; both elemental analysis and IR spectra reveal that the end groups must be predominantly ketone. All the polymers prepared here have C/N ratios greater than $2 + y$ (C/N in an infinitely long polymer), indicating carbonyl end groups. This is corroborated by the presence of a band at 1690–1695 cm^{-1} in the IR spectrum. The elemental analysis can also be used to estimate the polymer chain length via an end-group analysis. These results are also shown in Table I.

The IR spectra of all of these polymers are quite similar. The polymers with larger y show three sharp and distinct bands in the C–H stretching region near 2800–3000 cm^{-1}, but as the number of propyl groups decrease the intensity and resolution in this region decreases significantly. All of the polymers show a C=O stretch at 1692 ± 5 cm^{-1} with varying intensity, depending on the chain length of the polyazine: shorter chain (as determined by the elemental analysis) polymers have more prominent carbonyl bands, as expected. The C=N stretch is found at 1587 ± 5 cm^{-1} in all the polymers, again all the same within experimental error. The sharp C–CH$_3$ symmetric deformation is found at 1360 ± 2 cm^{-1} for all the polymers except $y = 1$, which is broader with several shoulders and the peak maximum is at 1350 cm^{-1}. Finally, all the polymers have a strong band at 1122 ± 3 cm^{-1} that we have assigned to the N–N stretch. The similarity of the IR spectra for this sequence of polyazines shows that the nature of the alkyl substituent groups along the chain have little effect on the structure of the polymer backbone.

The solution ^{13}C spectra of these polymers (only polymers with y = 1, 0.50, and 0.232 were sufficiently soluble to obtain spectra in a reasonable amount of time) are also all quite similar. In the solid state, the permethyl polymer ($y = 0$) has two resonances,[3d,3e] at 12.6 ppm from the methyl groups and at 155.2 ppm due to the imine carbons. As discussed more completely elsewhere,[5] the propyl–methyl polyazine ($y = 1$) has peaks that can be readily assigned to each type of carbon in the polymer but the NMR peaks show up in pairs, reflecting the fact that the sequencing of methyl and propyl substituents is not controlled in the synthesis (i.e., along the backbone the alkyl groups can be $R_1R_2R_1R_2$ or $R_1R_2R_2R_1$). For $0 < y < 0.5$, there can only be one type of propyl group: this is reflected in the NMR spectra of the $y = 0.50$ and $y = 0.232$ materials where peaks are found at 12.8, 13.0, 14.5, 20.4, and 29.0 ppm in the alkyl region. The peaks at 14.5, 20.4, and 29.0 ppm are assigned to the propyl group while the pair of peaks at 12.8 and 13.0 ppm are assigned to the methyl groups. The relative intensity of the peak at 13.0 ppm decreases with decreasing y, so that this must be the methyl group adjacent to the propyl group, while the peak at 12.8 ppm is due to methyls adjacent to other methyls. Similar conclusions are drawn from the ^1H spectrum, although the resolution of the two types of methyl peaks is considerably poorer.

The imine region of the spectrum is considerably more complicated. At least six different imine carbons can be resolved, even in the $y = 0.232$ material. These peaks are grouped into a set near 159 ppm, due to imine carbons with propyl substituents, and a set near 155 ppm, due to imine carbons with methyl substituents. The influence of the conjugated π system allows the imine carbons to be affected by the substitution pattern farther down the chain; thus, the imine region is a sensitive probe of the substitution sequence in these polymers.

Iodine doping of all these polymers is in progress. The solubility of the low y polymers is sufficient to make very thin films for both doping and optical spectroscopic experiments. The results of these investigations will be reported later.

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(6) In all the syntheses reported here, 1.0 g (0.0088 mol) of 2,3-butanedione dihydrazone was added to a solution of 0.5 mL of glacial acetic acid in 5.0 mL of *n*-butanol and heated to about 50 °C. The mixture of diones in 5.0 mL of *n*-butanol was added dropwise over about 10 min, and then the entire reaction was brought to reflux and maintained for 24 h. This was then cooled on ice, vacuum filtered, and vacuum dried for 1 day.

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CORRECTION

Abaneshwar Prasad and Leo Mandelkern*: Equilibrium Dissolution Temperature of Low Molecular Weight Polyethylene Fractions in Dilute Solution. Volume 22, Number 2, February 1989, p 914.

In our recent analysis of the crystallization kinetics of low molecular weight polyethylene fractions,[1,2] we inadvertently committed an error by utilizing nucleation theory pertinent to monomeric systems rather than the proper one for chains of finite molecular weight.[3–6] Since for long chains the complete molecule does not participate in the nucleation act, the appropriate expression for the free energy of fusion, which appears in the formation of critical size nucleus, is that of the infinite molecular weight chain, corrected for end-group effects.[5,6] In reanalyzing the kinetic data, we have taken a reasonable set of values for the nucleation interfacial free energy[5,6] and 118.6 ± 2 °C for the equilibrium dissolution temperature of polyethylene in *p*-xylene.[7]

For the fraction previously analyzed, $M_w = 3100$, $M_N = 2900$, the new results are independent of the value chosen for σ_e and are essentially the same as those originally reported.[1] Plots of $\ln G$ against the required temperature function yield straight lines of increasing slope for $v_2 = 0.001$–0.01. Two intersecting straight lines, which are consistent with a regime I–II transition, result for $v_2 = 0.05$.

We are now also able to analyze the data that were given for the fraction $M_w = 4050$, $M_N = 3900$.[2] In this case the results are similar to those recently found for dononacontahectane, $C_{192}H_{386}$,[6] in that the data can be represented by three intersecting straight lines. The slopes of the straight lines representing the high- and low-temperature regions are very close to one another. These results are also reminiscent of regime crystallization.

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