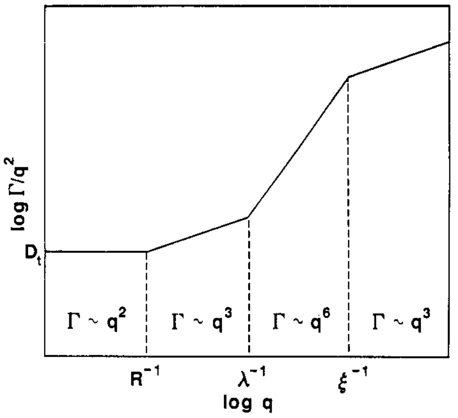

Figure 4. The scaling prediction for the relaxation rate in bimodal solutions gives three distinct regimes for $qR > 1$. The first is a third-power mean field Zimm behavior, where the solution viscosity moderates the relaxation times. The second is a sixth-power reptation regime, and the third is the small length scale Zimm regime, where relaxation processes are moderated by the solvent viscosity.

Table I

ϕ	R	λ	ξ	γ	β
$N^{1/2}/P$	$N^{1/2}$	$\xi(\eta_p/\eta_0)^{1/3}$	ϕ^{-1}	3	3
$(N^{1/2}/P)^{8/5}$	$N^{1/2}\phi^{-1/8}$	$\xi(\eta_P/\eta_0)^{1/3}$	$\phi^{-3/4}$	15/8	3
$(N^{2/5}/P)^{4/3}$	$N^{3/5}$	$\xi(\eta_p/\eta_0)^{1/2}$	$\phi^{-3/4}$	9/4	2

unity each of these functions is a simple constant.The Stokes–Einstein/reptation crossover is described by the function $f(x \gg 1) \sim x^{\gamma}$. The self-diffusion/configurational diffusion crossover is given by $g(x \gg 1) \sim x$, a well-known scaling result. The Zimm/reptation crossover is described by $h(x \gg 1) \sim x^{\beta}$, and the reptation/Zimm crossover is given by $k(x \gg 1) \sim x^{-\beta}$. The exponents and crossovers are in Table I for good and Θ solvents and for good-solvent ternary systems where excluded volume interactions are not necessarily screened.

The concept of a second Zimm regime is not new but was originally suggested by Richter et al.[18] to interpret inelastic neutron scattering data from unimodal polymer solutions. The "incomplete" hydrodynamic screening model they proposed, however, predicts a Zimm/Rouse/Zimm crossover, whereas the current model, which more fully accounts for entaglement effects, is Zimm/reptation/Zimm. Further experimental work is needed to distinguish between these possibilities.

In conclusion, dynamic light scattering measurements of configurational diffusion of optically labeled chains in semidilute solution are shown to be described by a modified Zimm model were the solution viscosity replaces the solvent viscosity. Based on this observation, a scaling theory is given for the internal dynamics in semidilute soltuion.

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Registry No. PS, 9003-53-6; PVME, 9003-09-2; toluene, 108-88-3.

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Thermal Decomposition of Poly(γ-methyl L-glutamate)

Recently our research efforts have focused on the thermal decomposition behavior of the side chains of polymers.[1] The side chain of poly(γ-methyl L-glutamate) (PMLG) is expected to influence the thermal decomposition more than the skeletal chain stabilized by hydrogen bonds.[2–5] There are a few studies[6–8] on the thermal decomposition of poly(glutamic acid) esters, but the reaction mechanism is hardly discussed. In the present communication, we propose a thermal decomposition mechanism for PMLG and give some supporting evidence for it.

The PMLG samples were cast from 1.2-dichloroethane. The solution of PMLG (Ajicoat A-2000) was kindly supplied by Ajinomoto Inc. Methyl *n*-butyrate and γ-methyl L-glutamate (MLG), used to elucidate the thermal decomposition mechanism of PMLG, were synthesized in the usual way.[9] The investigation of the thermal decomposition in a flow of helium was carried out by pyrolysis gas chromatography (GC)–mass spectrometry (MS). Details of pyrolysis GC–MS are given elsewhere.[10]

Figure 1 and Table I show results of pyrolysis GC–MS on PMLG at 570 and 770 K. Products 1, 4, 5, and 6 are identified as carbon dioxide,[11] methanol, methyl acetate, and methyl acrylate, respectively. Product 2 is perhaps a mixture of light gases such as methane ($m/z = 16$), ethene ($m/z = 28$), ethane ($m/z = 30$), propene ($m/z = 42$), and propane ($m/z = 44$). Water appears above 58 min in pyrogram I; the GC column filler used in the present experiment, DC-550, may have little effect on water. Products 7–10 are unknown, but we regard them as decomposition products due to radical scission of the skeletal chain, since they evolve at 770 K but do not evolve at 570 K. Product 3 was identified as 1,2-dichloroethane, the solvent for Ajicoat A-2000.

Generally, esters undergo nucleophilic substitution at their acyl carbons by reacting with primary or secondary amide.[12,13] Pyrolysis GC–MS data on MLG are shown in Figure 2. The major decomposition products are carbon dioxide, methanol, and 2-pyrrolidone. Liberation of

Table I
Relative Intensities in Mass Spectra of Thermal Decomposition Products of PMLG and Pure Compounds

mass number (m/z)	relative intensity: product 1	CO_2[a]	product 4	CH_3OH	product 5	CH_3COOCH_3	product 6	CH_2=$CHCOOCH_3$
12	18	23						
15			63	66	72	80	43	44
16	24	30						
22	1	1						
26							32	36
27							100	100
28	33	34						
29			87	95	32	26		
31			100	100				
32			61	58				
42					13	17	18	23
43					100	100		
44	100	100						
55							92	95
59					6	7		
68							3	4
74					8	10		
85							8	9

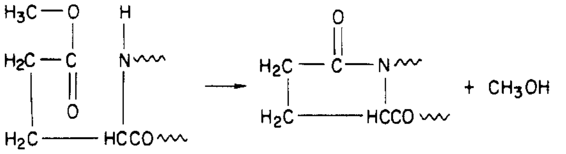
[a] Reference 11. Product numbers correspond to peak numbers in pyrograms of PMLG.

Table II
Relative Intensities in Mass Spectra of Thermal Decomposition Product 2 of PMLG and Pure Compounds

mass number (m/z)	product 2	relative intensity[a]: CH_4	C_2H_6	C_2H_4	C_3H_8	C_2H_6	CO_2
13	11	18		4		2	
14	16	29	4	6	2	4	
15	33	95	5		6	5	
16	38	100					30
26	23		23	62	9	11	
27	45		33	65	39	38	
28	100		100	100	59	1	34
29	48		22	2	100		
30	12		26		2		
37	13				3	14	
38	16				5	19	
39	36				17	71	
40	15				3	29	
41	35				13	100	
42	24				6	68	
43	18				23	2	
44	86				29		100

[a] Intensities of pure compounds are given in ref 11.

methanol from PMLG is considered to result from the following reaction:



(I)

Figure 3 shows IR spectra of the residue of PMLG decomposed at 770 and 500 K and of virgin PMLG. The absorptions were assigned by reference to the literature.[14] Decreases in the intensity of absorptions due to C–H stretching of methyl (2960 cm^{-1}) and C=O stretching of ester (1750 cm^{-1}) with increasing temperature mean liberation of methanol by reaction I. The absorption intensities due to N–H stretching (3300 cm^{-1}), N–H deformation (1550 cm^{-1}), and C=O stretching of amide (1660 cm^{-1}) also decrease with increasing temperature. These results suggest that the skeletal chain undergoes the carbonization reaction soon after reaction I. Actually there was about 20% charred residue in the thermal decomposition even at 770 K.

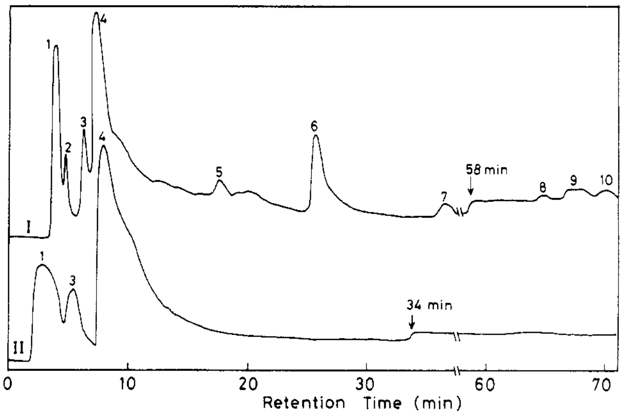
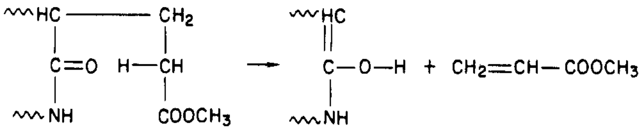


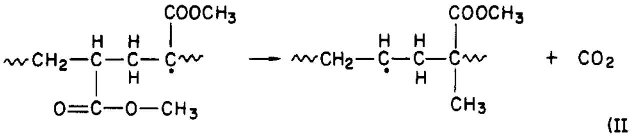
Figure 1. Pyrograms of thermally decomposed PMLG: (I) at 770 K; (II) at 570 K. GC column: packing, DC-550/15% 60–80 mesh Chromosorb W; size, 4 m × 4 mm; heating rate, 2 K/min. GC carrier gas: helium. GC detector: NEVA TE-600 mass spectrometer; total emission current (current between the ion chamber and the repeller), 213 μA; electron energy (potential between the filament and the repeller), 70 V; ion energy (potential between the ion chamber and the earth), 12 V. The thermal decomposition was carried out in helium used as a GC carrier gas.

A nonradical reaction through a six-membered-ring transition state is speculated for the evolation of methyl acrylate by analogy with the thermal decomposition mechanism of poly(vinyl acetate).[15,16]



However, no methyl acrylate peak appears in the pyrogram of PMLG decomposed at 570 K, as shown in Figure 1. The evolution at 770 K and no evolution at 570 K for methyl acrylate suggest a radical reaction mechanism for the evolution of methyl acrylate.

Several investigators[17,18] have presented the following mechanism for the evolution of carbon dioxide in the thermal decomposition of poly(methyl acrylate):



(II)

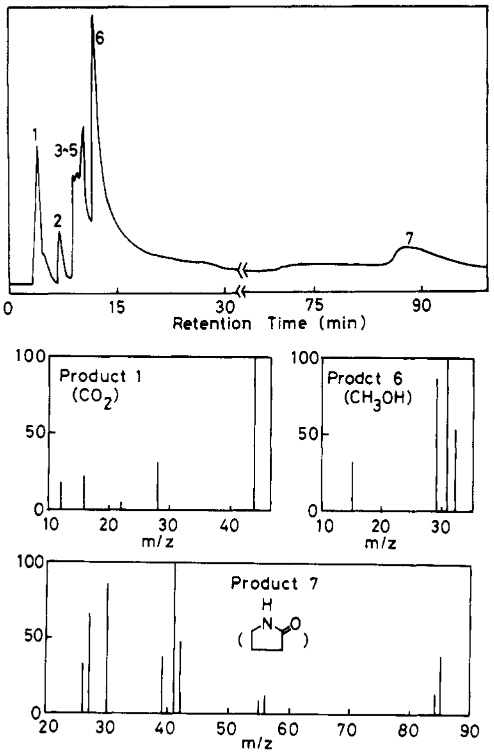


Figure 2. Pyrolysis GC-MS data on MLG at 770 K: Pyrolysis GC-MS techniques were carried out under the same conditions as described in the caption of Figure 1. The heights of the bars in the mass spectra express the relative intensity. The products were identified as the compounds in parentheses.

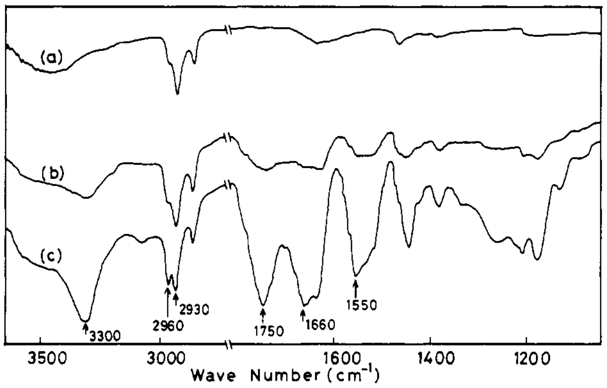
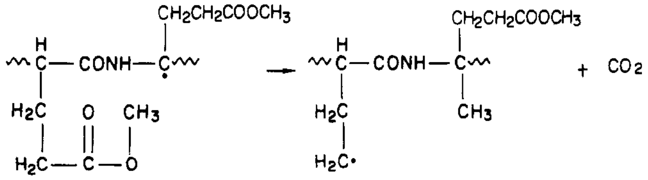
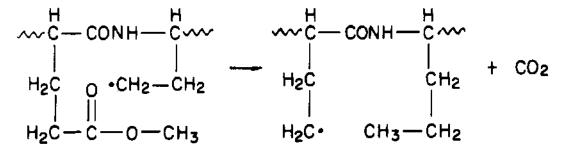


Figure 3. IR spectra of the residue of thermally decomposed PMLG: (a) at 770 K; (b) 500 K; (c) virgin PMLG. IR techniques: apparatus, Hitachi 285 IR spectrometer; sample, KBr disk.

By analogy with reaction II, the mechanism of evolution of carbon dioxide from PMLG is considered to be the reaction

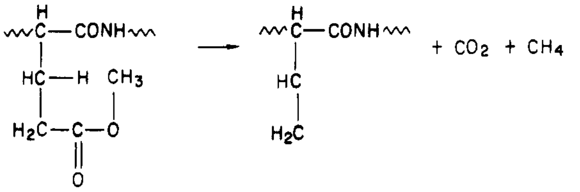


The resulting radical is hydrogenated to propyl substituent:



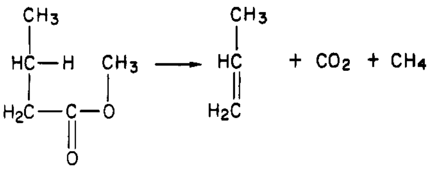
(III)

This radical reaction should be possible only at higher temperatures. Carbon dioxide, however, evolves even at lower temperatures (see pyrogram II in Figure 1). It suggests that the decarboxylation reaction at lower temperatures proceeds by a nonradical reaction. Here we propose for the decarboxylation the following reaction mechanism involving a six-membered-ring transition process:



(IV)

The pyrolysis GC-MS on methyl *n*-butyrate with the six-membered-ring structure resulted in the evolution of carbon dioxide, methane, and propene, which proves the six-membered-ring process in the thermal decomposition:



These results support reaction IV.

Conclusions about the reaction mechanism proposed for the thermal decomposition of PMLG are summarized as follows: (1) At a decomposition temperature of 570 K, methanol and carbon dioxide evolve by reactions I and IV, respectively. Both reactions are nonradical. (2) At a decomposition temperature of 770 K, radical reactions are dominant, though both reactions I and IV are considered to occur. Methyl acetate and methyl acrylate evolve only by a radical scission reaction.

Registry No. PMLG, 25086-16-2; Ajacoat A-2000, 25036-43-5; γ-methyl L-glutamate, 1499-55-4; carbon dioxide, 124-38-9; methanol, 67-56-1; methyl acetate, 79-20-9; methyl acrylate, 96-33-3; 2-pyrrolidone, 616-45-5.

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Fractal Dimension of a Cross-Linking Polymer at the Gel Point

Many models have been proposed to describe cross-linking polymers at their gel point. The most accepted ones are based on the classical theory of Flory,[4,5] Stockmayer,[6] and Zimm[7] and on the percolation model.[8-10]

The fractal dimension d_f of a molecular cluster is defined by

$$R \sim M^{1/d_f} \tag{1}$$

where R is the radius of gyration and M is the molecular weight. The fractal dimension at the gel point was found to be[10]

$$d_f = 4, \qquad \text{Zimm–Stockmayer (Cayley tree)} \tag{2a}$$

$$d_f = 2.5, \qquad \text{percolation cluster at threshold} \tag{2b}$$

However, recent computer modeling[11] of the kinetic gelation suggests that a different value for d_f should be expected.

Recently, a theory[3] has been derived for predicting the frequency dependence of the complex viscosity in terms of the arbitrary fractal dimension of the molecular cluster. In the regime of large molecular weights where both the hydrodynamic and excluded volume effects are fully screened, the frequency dependence of the viscosity is shown to be

$$\eta^*(\omega) \sim \omega^{-2/(d_f+2)}, \qquad 0 < \omega \tag{3a}$$

$$\eta^*(\omega) \sim M^{2/d_f}, \qquad \omega \to 0 \tag{3b}$$

This theory has been compared to experimental observations and is known to reproduce the high-concentration behavior of unentangled linear polymers. It makes it possible to draw conclusions regarding the global structures of polymeric systems from measurements of the complex viscosity as a function of frequency.

Chambon and Winter[1] measured the evolution of the rheological behavior during the cross-linking of polymers, using stoichiometrically balanced poly(dimethylsiloxane) (PDMS) as a model polymer in which two-functional and four-functional molecules end-linked by hydrosilation reaction. A discrete set of stable samples represented the continuous evolution of the cross-linking reaction. The samples were prepared by poisoning the catalyst at several different extents of reaction. For the rheological experiments it was important that the samples were cross-linked at rest and, therefore, had no memorized flow history. The molecular weights of the prepolymers were below the entanglement limit to reduce the effect of physical entanglements.

The storage modulus G' and the loss modulus G'' have been measured as a function of frequency, applying time–temperature superposition to stretch the frequency range to about 5 decades. At low extent of reaction, the storage modulus was smaller than the loss modulus, $G' < G''$. With increasing extent of reaction, the two moduli increased in value and became more similar until, at a critical extent of reaction, they were found to completely grow together. At this state of the material, the storage and the loss moduli were congruent functions and they could be described by a "power law"

$$G'(\omega) = G''(\omega) = A\omega^{\alpha}, \qquad \alpha = \tfrac{1}{2} \tag{4}$$

where A is a material constant. Winter and Chambon[2] hypothesized that the power law relation is valid not only in the experimental region but in the entire frequency range $0 < \omega < \infty$. On the basis of this hypothesis, the Kramers–Kronig relation gives $\alpha = {}^1/_2$ as the *only* possible value for the exponent. Beyond the critical extent of reaction, the storage modulus was always larger than the loss modulus, $G' > G''$, over the entire frequency range.

Winter and Chambon[2] could also show that the one sample which exhibited congruent behavior was at the phase transition from viscoelastic liquid to viscoelastic solid. We therefore know that the complex viscosity

$$\eta^*(\omega) = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2} \tag{5}$$

of the PDMS at the gel point is

$$\eta^*(\omega) = A\omega^{-1/2} \tag{6}$$

Comparison of eq 3 and 6 gives the result that the fractal dimension of the PDMS cluster at the gel point is

$$d_f = 2 \tag{7}$$

Although the dimension of the percolation cluster at the percolation threshold is closer to this value than the dimension of the Cayley tree of the classical theory, it seems that the cluster at the gel point is not a percolation cluster at the threshold. The fractal dimension at the gel point is the same as that of an isolated linear chain of infinite length under Θ-conditions. This is surprising because the polymer at the gel point is a highly branched macromolecule. Furthermore, it is to be pointed out that the experimental observation[1,2] of the congruency $G' \sim \omega^{1/2} \sim G''$ at the gel point is a direct manifestation of the fractal dimension of the system although this behavior is reminescent of the Rouse spectrum valid for an isolated linear flexible chain of infinite length.

Although the Rouse model of networks also predicts $G' \sim \omega^{1/2} \sim G''$ for intermediate frequencies, the standard arguments[12] show that this intermediate frequency range is restricted to less than a decade for molecular weights between cross-links employed in ref 1 and 2. This is to be contrasted with the observed congruency (eq 6) over more than 5 decades in frequency.

Since the molecular weight of the growing cluster diverges at the gel point, the experimental complex viscosity at $\omega = 0$ also diverges, in accordance with eq 3.

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