activated. Thus, two aluminum porphyrin molecules participate in the polymerization (Scheme I).

By the virtue of such activation, the polymerization initiated with (TPP)AlOR is remarkably accelerated by the addition of (TPP)AlCl which itself cannot initiate the polymerization. The acceleration of polymerization by the addition of (TPP)AlCl is also observed in the polymerization of ε-caprolactone and D-lactide ((3(R), 6(R)-3,6-dimethyl-1,4-dioxacyclohexene-2,5-dione) initiated with (TPP)AlOR. For example, in the polymerization of D-lactide (9.33 mmol) initiated with (TPP)AlOMe (0.14 mmol) in CH_2Cl_2 (4.9 mL) at 100 °C for 2 h, the conversion was 26.1%, while upon addition of an equimolar amount of (TPP)AlCl to (TPP)AlOMe the conversion increased to 39.6%.

In conclusion, the results of the present study provide evidence that two metal atoms participate in the polymerization of lactone, and probably epoxide, with other organometallic catalyst systems as well.

Registry No. 1 (X = Cl), 71102-37-9; 1 (X = OMe), 66945-43-5; 2, 542-28-9; 2 (n = 4, homopolymer), 26354-94-9; 2 (n = 4, SRU), 26499-05-8.

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Notes

Number of Entanglement Strands per Cubed Tube Diameter, a Fundamental Aspect of Topological Universality in Polymer Viscoelasticity

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Polymer viscoelastic properties are strongly influenced by polymer chain entanglement. A strong indication of this is the modulus plateau that can be observed for nearly monodisperse high molecular weight (MW) samples.[1-3] Modeling chain entanglements as slip-links and chain diffusion as reptation,[4] Doi and Edwards[5-8] developed a very successful constitutive equation for monodisperse linear polymers in 1978. The deficiency of the Doi–Edwards theory to explain fully the experimentally observed MW dependence of the zero-shear viscosity ($\eta \propto M^3$ for theory; $\eta \propto M^{3.4}$ for experiment) has been removed by a proposed general linear viscoelastic theory.[9] An extensive quantitative line-shape analysis of the linear viscoelastic spectra has further strongly supported the validity of the proposed general theory.[10-12] It has been shown that the general theory is universal for all linear flexible polymers as long as the MW is expressed in terms of the reduced unit (M/M_e, where M_e is the entanglement MW). A constitutive equation[13] including the chain tension relaxation process[14] has been obtained from modifying the Doi–Edwards theory. It has been shown from analyzing experimental results in terms of the constitutive equation that the melt flow instability, i.e., slip–stick melt fracture, is a universal phenomenon for all linear flexible polymers.[13] It will occur to a polymer as long as its M/M_e value is high

enough and its molecular weight distribution (MWD) is narrow enough. The proposed general linear viscoelastic theory and constitutive equation are unified in the terminal region.[15]

All these results summarized above support the universality of the topological constraint effect as described by the tube model, where the tube diameter, a, is equivalent to the distance between two adjacent slip links (entanglements). Then we ask the question whether there is a universal relation among the basic elements (physical quantities) in the tube model as described by Doi and Edwards. A similar motivation has led Graessley and Edwards[16] to propose a correlation among the basic elements.

The key elements in the tube model should be the bulk density of the polymer, the entanglement MW, the mass and length associated with each Kuhn segment, and the tube diameter. A difficulty encountered here is the lack of experiment to determine the Kuhn segment length and mass independently. Graessley and Edwards[16] used $l = C_\infty b$ (C_∞ is the characteristic ratio and b is the average length of the main chain chemical bonds of the average mass, m) for the Kuhn step length. There should be an approximation involved in their approach.

Here, we study this matter from a different viewpoint. Without linking the Kuhn segment with the characteristic ratio (C_∞) directly, we use the C_∞ value to calculate the tube diameter from the entanglement MW through the following equation[17]

$$a^2 = C_\infty \frac{M_e}{m} b^2 \tag{1}$$

This equation is totally consistent with the Doi–Edwards

Table I
Number of Entanglement Strands per Cubed Tube Diameter, n_t, for the Listed Polymers[a]

	T	ρ	$G_N \times 10^{-7}$	M_e	C_∞	b	a	m	n_e	n_t
polystyrene	400	1.007	0.2	13500	9.4	1.54	76	52	259	19.7
poly(α-methyl styrene)	473	1.04	0.32	10225	10.1	1.54	64.4	59	173	16.4
polybutadiene (high cis)	298	0.9	0.76	2347	4.9	1.47	43	13.5	174	18.2
polyisobutylene	298	0.89	0.25	7056	6.2	1.54	61	28	252	17.1
polyisoprene (high cis)	298	0.9	0.44	4054	5.3	1.47	52	17	238	19
hydrogenated polyisoprene	298	0.854	1.15	1472	6.8	1.54	36.8	17.5	84	17.5
poly(vinyl acetate)	330	1.14	0.36	6950	9	1.54	58.7	43	162	20
polybutadiene, $\chi_{12} = 0.08$	300	0.896	1.25	1430	5.1	1.47	33.4	14.1	101	14.5
polybutadiene, $\chi_{12} = 0.43$	289	0.9	0.93	1860	6.1	1.47	37.8	17.2	108	16.2
polybutadiene, $\chi_{12} = 0.99$	306	0.883	0.42	4280	7	1.54	51.6	26.7	160	17
polyethylene	373	0.802	2.7	737	7.2	1.54	30	14	52.6	17.7
hydrogenated polybutadiene, $\chi_{12} = 0.43$	338	0.832	1.1	1700	6.4	1.54	38.1	17.8	95.5	16.3
hydrogenated polybutadiene, $\chi_{12} = 0.99$	373	0.819	0.19	10694	5.5	1.54	71	27.7	386	16.5

av 17.4 ± 8%

[a] n_t is given by eq 4. The related quantities are as defined in the text. The G_N and C_∞ data of polystyrene are from ref 10 and 29, respectively. The data in the last six rows are from ref 30 and the rest from ref 16. The M_e values are calculated according to $M_e = {}^4/_5(\rho RT/G_N)$ (see ref 9 and 10). G_N is in units of dyn/cm^2; ρ is in g/cm^3; b and a are in Å.

theory, in which the polymer chain between two adjacent entanglements is Gaussian.

The plateau modulus of a polymer melt is proportional to the number of entanglement strands per unit volume n_v as given by

$$G_N = \frac{4}{5}\frac{\rho RT}{M_e} = \frac{4}{5}n_v kT \qquad (2)$$

where

$$n_v = \rho N/M_e \qquad (3)$$

ρ is the polymer density, N the Avogadro number, and k the Boltzmann constant. If the topological constraint effect associated with chain entanglement is universal, a certain one-to-one correspondence should exist between the size of the tube and n_v. A logical way is to calculate a quantity which is independent of dimension. This should be the number of entanglement strands per cubed tube diameter:

$$n_t = n_v a^3 = \frac{\rho N}{M_e}\left(C_\infty \frac{M_e}{m}b^2\right)^{3/2} \qquad (4)$$

n_t should be a universal constant if only the topological constraint effect is important. Every quantity in eq 4 can be determined independently. In Table I, these quantities as well as the n_t value calculated from eq 4 for 13 different polymers are listed. The n_t values have an average of 17.4 with a standard deviation of only 8%. Considering the difference of the M_e, C_∞, m, and/or n_e ($=M_e/m$) values among the polymers, the n_t value appears significantly constant. This result has a further theoretical basis as described below: Equation 4 can be rewritten as

$$G_N' a^3 = n_t kT \qquad (5)$$

where G_N' is the plateau modulus according to the theory of rubber elasticity and $G_N' = 5G_N/4$ as defined here (the factor 4/5 is due to the chain slippage[9,10] in the Doi–Edwards theory). This equation is very similar to the molecular form of the equation of state, $PV = nkT$, for an ideal gas. It has been recognized that there is a great deal of similarity between the ideal gas law and the theory of rubber elasticity.[18] The polymer chain configuration is indeed ideal in melt.[19] The similarity arises because the Gaussian function describes the distribution of states in both cases.[20] The tube diameter, a, is of sufficiently long distance (yet, the shortest characteristic length above the Kuhn segment), over which the Gaussian statistics of a chain section in the polymer melt is applicable.[6,21] Thus, it is logical to choose a^3 as the volume element.

With n_t being constant, eq 4 provides a link between M_e, which is the smallest molecular structure of important concern in polymer viscoelasticity, and C_∞, which is closely related to the microstructure of the polymer chain. Using the rotational isomeric state theory, successful calculations of C_∞ have been made.[17] In other words, eq 4 may have made an initial link between two fields of polymer research.

Assume that each Kuhn segment has the shape of a cylinder of length l and diameter d. The size of a Kuhn segment under consideration here contains the average contribution of free volume, which necessarily exists between segments. Taking the average number of strands per a^3 cube to be 18, we can have

$$(\pi/4)d^2 l N_e = a^3/18 \qquad (6)$$

where N_e is the number of Kuhn segments between two adjacent entanglements.

Using the relation $a = N_e^{0.5}l$, we obtain from eq 6

$$N_e = 200(d/l)^4 \qquad (7)$$

This simple result is fundamentally revealing. Equation 7 means that the N_e value is solely determined by and very sensitive to the aspect ratio l/d of the Kuhn segment. The thinner the Gaussian coil is, the smaller the N_e value. This is indeed very reasonable to expect. Since both the Kuhn segment and N_e are defined in a universal way without involving the detailed chemical structure of any polymer, it is possible that both the l/d and N_e values are universal constants.

It is interesting to point out two groups of polymers, whose n_t values are systematically lower than those listed in Table I. One group is the polymers that have oxygen atoms on their chain backbones: poly(dimethylsiloxane) (PDMS) and poly(ethyleneoxide) (PEO). Another is the methacrylate polymers. Their n_t values are listed in Table II. The dipolar moments on the PDMS and PEO chain backbones may give the polymer chains a significant structural interaction in addition to chain entanglement. As a result, PDMS and PEO may not need as large an N_e value to form an entanglement for the same aspect ratio of the Kuhn segment (see eq 7). The methacrylate polymers have carbonyl groups next to their chain backbones. Similar to the case of PDMS and PEO but to a less degree, the methacrylate polymers may have smaller n_t values because of the dipolar interaction associated with the carbonyl group. It seems necessary to have the dipolar groups on or close (next) to the chain backbones to make n_t smaller. Poly(vinyl acetate), whose carbonyl groups are farther away from its chain backbone, has a "normal" n_t value, listed in Table I. These results suggest that the

Table II
Number of Entanglement Strands per Cubed Tube Diameter, n_t, for Listed Polymers[a]

	T	ρ	$G_N \times 10^{-7}$	M_e	C_∞	b	a	m	n_e	n_t
poly(methyl methacrylate)	473–423	1.14	0.48–0.62	6176	8.7	1.54	50.5	50	124	14.3
poly(2-ethylbutyl methacrylate)	373	0.995	0.14	17632	9.1	1.54	66.9	85	207	10.2
poly(n-hexyl methacrylate)	373	0.95	0.087	27090	10.3	1.54	88	85	319	14.5
poly(n-octyl methacrylate)	373	0.927	0.033	69691	10	1.54	129	99	704	17.3
										av 14.08 ± 20%
poly(dimethylsiloxane)	298	0.97	0.24	8010	5.2	1.46	49	37	216	8.6
poly(ethylene oxide)	298	1.08		1500[b]	3.8	1.49	29.4	14.6	102	11

[a] The data are from ref 16. G_N is in units of dyn/cm^2; a and b are in Å. [b] Estimated from M_c.
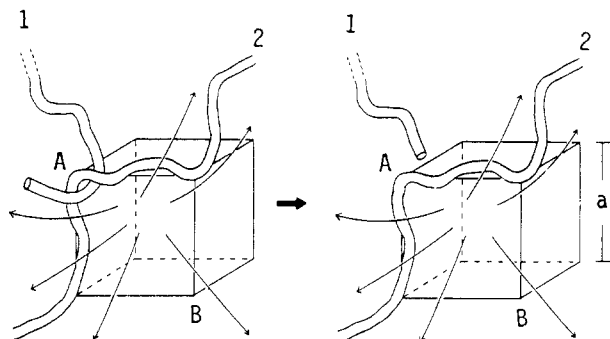
Figure 1. Curved arrows represent entanglement strands which emanate from the entanglement points inside the a^3 cube through the front square face (see text). As chain 1 reptates away and disentangles from chain 2, these entanglement strands prevent chain 2 segments from moving from position A to position B.

individual microstructure of a polymer chain can somewhat modify the universal topological chain behavior as depicted by the tube model. The microstructure may cause the small difference of the M_c/M_e ratio among different polymers[1,2] and the slightly stronger polymer concentration (C, the volume fraction) dependence of the plateau moduli than C^2 for certain polymers.[16,21]

In each a^3 there are about 18 entanglement strands. In other words, there are about nine entanglements (half of the number of entanglement strands) per a^3 cube. Each entanglement emanates four entanglement strands. It is reasonable to assume that each of the entanglement strands does not end at an entanglement inside the same a^3 cube. Then, in average, six entanglement strands pass through each of the six square faces of the a^3 cube. As schematically shown in Figure 1, these entanglement strands will serve as topological barriers to prevent a primitive path step (of a certain chain, whose ends are far from the concerned a^3 cube; for easy understanding, one can think that the primitive path step is on the lattice frame of the cube) from orienting into another direction, after a chain has reptated away (disentangled) from it. Consequently, the loss of stress anisotropy may arise only from the randomization of entanglement conformation of the single chain that reptates away (chain 1 in Figure 1).

Several tube renewal models[22–25] have been proposed by assuming basically that each disentanglement randomizes right away the orientation of a primitive path step of the tube and that the tube behaves as a "Rouse tube". Clearly, these models have not recognized the high level of topological barriers in each a^3 cube as discussed above. In terms of the cage picture, as often used in the tube renewal models, instead of one, about six interpenetrating cubic lattices are required to reflect the situation in the polymer melt.

On the other hand, the present result explains the conclusion that the tube renewal process is negligible as long as the MWD i. very narrow, which has been drawn from an extensive quantitative line-shape analysis of linear viscoelastic spectra of nearly monodisperse polystyrene

samples in terms of the proposed general theory.[9–12] In the case of binary blends consisting of two far separated nearly monodisperse components, however, the tube renewal effect on the high MW component caused by the relatively fast reptation motion of the low MW chains is clearly visible. A model to explain this tube renewal process and its effect on the blending law has been proposed.[26] The model is compatible with the conclusion described above for the nearly monodisperse samples.

Consistent with the viewpoint given in this paper, the characteristic time of the tube renewal process (imparted upon the high MW component by the low MW component) in a binary blend is much larger (about 7 times) than the reptation time of the low MW chain.[26]

For the concentrated polymer solutions, the number of entanglement strands per cubed tube diameter (denoted as n_t') decreases with dilution. Similar to eq 6, we can write for the solution

$$(\pi/4)d^2lN_e' = a'^3C/n_{t'} \tag{8}$$

where N_e' and a' are the number of segments in an entanglement strand and the tube diameter, respectively, for a polymer solution.

Using the relation $N_e' = N_eC^{-1}$.[1,2,21,22] in the concentrated solution regime, we can show from eq 8 that

$$n_t' = n_tC^{0.5} \tag{9}$$

At sufficiently low concentration, the n_t' value may be so low that the tube renewal process will become important, even though the polymer is nearly monodisperse.

It has been suggested that in the semidilute regime with a good solvent, N_e' and a' scale with concentration in the same way as the number of segments g and length ξ associated with each "blob", respectively.[27,28] That is,

$$N_e' \propto C^{-1.25} \tag{10}$$

and

$$a' \propto C^{-0.75} \tag{11}$$

Using these two relations in eq 8, it can be shown that the number of entanglement strands per cubed tube diameter is independent of concentration in the semidilute regime. This also suggests that the number of blobs per cubed tube diameter is independent of concentration in the semidilute regime, because, as implied in eq 10 and 1', the number of blobs per entanglement strand is a constant.

It has been argued that in the semidilute regime osmotic pressure (π) and elastic modulus (E) (at the short time before the terminal region) should both be proportional to the concentration of binary polymer–polymer contacts.[27,28] That is,

$$\pi \text{ (or } E) \propto C^{2.25} \propto kT/\xi^3 \text{ (or } kT/a'^3) \tag{12}$$

Relation 12 also means that the number of blobs or entanglement strands per cubed tube diameter is independent of concentration. Thus, eq 8 as applied in the

semidilute regime using eq 10 and 11 is equivalent to relation 12.

In summary, from the viscoelastic data available in the literature, the numbers of entanglement strands per cubed tube diameter for different linear flexible polymers are calculated. In agreement with the expectation based on the universality of the tube model, the obtained n_t values are very constant. This supports that the topological effect as described by the tube model is dominant in affecting the viscoelastic properties of polymers. In the semidilute regime, chain entanglement is greatly influenced by the thermodynamic property: excluded volume effect, in the solution. In the melt (and the concentrated region), packing the space with polymer segments (and solvent molecules) appears to be the dominant factor in determining chain entanglement as suggested by eq 7.

With n_t being constant, a link between polymer viscoelastic behavior and polymer chain microstructure has been made.

The result that n_t is quite large explains the conclusion that the tube renewal process is negligible as long as the MWD is very narrow, which was previously drawn from the linear viscoelastic spectrum line-shape analyses.

Note. The main idea presented in this paper is quite different from that of Graessley and Edwards. A Referee pointed out "A consequence (of the Graessley–Edwards analysis) is that a melt of a bulky polymer with large side groups should behave the same as a less bulky polymer at somewhat less than melt concentration. Thus the Graessley–Edwards analysis would lead one to expect essentially no dependence of n_t on C in the concentrated regime, in contradiction to eq 9". Some readers may have a similar question. The answers to the Referee's comments listed below, I think, would help explain why this work and what are the possible defects in the Graessley–Edwards analysis.

(1) As explained in the main text, the Graessley–Edwards relation is, at best, an approximation.

(2) The present correlation (eq 4) is much stronger than that of Graessley and Edwards. Compared to experimental results, their relation has a standard deviation of ~30% (see Table I of ref 16); while it is only 8% in the present case.

(3) The connection between melts and concentrated solutions, which the referee pointed out as the main thrust of the Graessley–Edwards analysis, is in fact not that well supported by the experimental results. One can easily draw a straight line with a slope as large as 3 or higher (the a value of eq 4 of ref 16) through the more reliable data points (mainly those of the hydrocarbon polymers) in Figure 1 of ref 16. On the other hand, the a value in the concentrated solution systems is typically between 2 and 2.3. (from the relation $G_N \sim C^a$). This large discrepancy is, of course, related to the two previous points.

(4) The tube diameter can be calculated from the entanglement molecular weight (which is calculated from the measured plateau modulus, density, and temperature) and the characteristic ratio; and thus is a well-defined, fundamental, physical quantity in the Doi-Edwards theory. This quantity is totally missing in the Graessley–Edwards relation (eq 4 of ref 16). This seems quite inconsistent with the success of the Doi–Edwards theory.

Note Added in Proof. From L. J. Fetters, I have received a collection of data twice as large as that in Table I, much of which is unpublished and has been accumulated over years with his co-workers. They have calculated the n_t values from their data and confirm the conclusion that n_t is topologically a universal constant. Their results are being prepared for publication (private communication).

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Nitroso Spin Labeling of Polymers Containing Main Chain Double Bonds: An Electron Spin Resonance Study

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Introduction

The synthesis and ESR spectroscopy of nitroxyl-labeled polymers have received considerable attention during the last 15 years. The methods of preparation and the possible applications have been reviewed by Törmälä,[1] Miller,[2] and recently by Cameron and Bullock.[3] The most frequently used method for bonding a stable radical center of nitroxyl type to a polymer backbone or side chain is based on the

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