

Elastic Behavior of Concentrated Solutions of Acrylonitrile Copolymers

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Synopsis

The elastic behavior of concentrated solution of acrylonitrile copolymer was investigated by the capillary end correction method. The results were as follows. (1) The shear stress is proportional to recoverable shear strain in accordance with Hooke's law below critical concentration; above a critical concentration, however, the shear modulus depends on shear stress. (2) The log-log plots of zero shear modulus against polymer concentration and molecular weight fall on two straight lines with different slopes. The intersection of lines is considered to be the onset of elastically deformable entanglement network. We denote this inflection point as $(C_e)_e$ or $(M_e)_e$. (3) The log-log plot of viscosity against polymer concentration does not show a change of slope at the critical concentration $(C_e)_e$. (4) By the application of the kinetic theory of rubberlike elasticity to the pseudo-network structure of concentrated polymer solution, in the range of $C_e < C < (C_e)_e$ or $M_e < M < (M_e)_e$, the number of chain entanglements per molecule is kept one; moreover, in the range of $C > (C_e)_e$ or $M > (M_e)_e$, the number of chain entanglement increases to three.

INTRODUCTION

The viscosity of polymer melts or concentrated solutions of polymers has been well investigated by many authors. Plots of the low-shear viscosity η_0 of concentrated polymer solutions against molecular weights of polymers and polymer concentrations exhibit rapid increases in viscosity η_0 at a critical molecular weight of polymer M_e and polymer concentration C_e . It has been postulated that polymer molecules start to become entangled and form a continuous network structure at a critical molecular weight of polymer M_e and polymer concentration C_e .^{1,2}

On the other hand, our previous study on concentrated solutions of acrylonitrile copolymer³ indicate the existence of another entanglement network that is elastically deformable.

Recently, Schreiber et al.⁴ also reported on an elastically deformable entanglement network. They call the onset of melt elasticity the critical molecular weight $(M_e)_e$. We also denote the critical polymer concentration $(C_e)_e$ as an onset of solution elasticity. The value of critical polymer concentration $(C_e)_e$ is experimentally determined by plotting shear modulus against polymer concentration, by analogy with a plot of the viscosity η_0 versus polymer concentration C for determining C_e .

In this paper, the shear moduli of polymer solutions of acrylonitrile copolymers having different molecular weights were determined by separating the component from viscoelastic flow, based on the procedure proposed by Bagley,⁶ who showed that the end correction on capillary extrusion could be separated into two components such as Couette correction and recoverable shear strain.

EXPERIMENTAL PROCEDURE AND PRINCIPLES

Principles of Shear Modulus Determination

When a concentrated polymer solution is forced to flow from a reservoir through a capillary of radius R and length L , the shear stress at the rim of the capillary is usually computed from the equation

$$\tau_R = P_T R / 2L \quad (1)$$

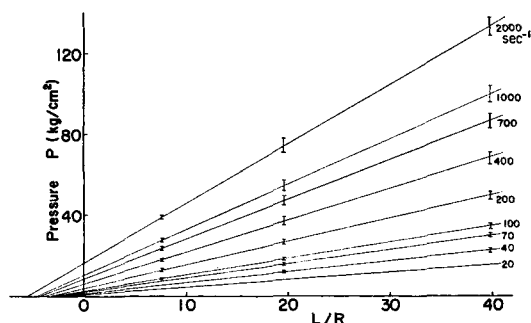


Fig. 1. Pressure P vs. capillary dimensions (L/R) in 54.1% solution of acrylonitrile copolymer of $M_w 7.0 \times 10^4$ in aqueous NaCNS solution at 120°C .

where P_T is the applied pressure differences across the ends of capillary. If we call P_T the total pressure, P_c the equilibrium pressure inside the capillary, ρ the density of the solution, and V the mean velocity of flow, we can write, with m as a constant coefficient:

$$P_T = P_c + m\rho V^2 \quad (2)$$

Philippoff and Gaskins⁷ showed that the energy balance for the capillary could be written as:

$$\begin{aligned} P_T Q &= P_c Q + m\rho V^2 Q + E \\ P_T &= P_c + m\rho V^2 + E/Q \\ P_T &= P_c + m\rho V^2 + (P_{11})_R \end{aligned} \quad (3)$$

where E is elastic energy transported out of the capillary (in ergs), E/Q is the mean elastic energy (in ergs/cubic centimeter or dynes/square centimeter), or the axial normal force, P_{11} . Any real "geometrical end cor-

rection" increases the active length of capillary by $\delta L = nR$. n is termed the Couette correction.

$$P_c = [2(L + \delta L)/R]\tau_{cR} = [2(L + nR)/R]\tau_{cR} \quad (4)$$

where τ_{cR} is the corrected shear stress at the wall taking into account both the geometrical end effect and the elastic energy. Furthermore, at radius R :

$$(P_{11})_R = \tau_{cR}S_R \quad (5)$$

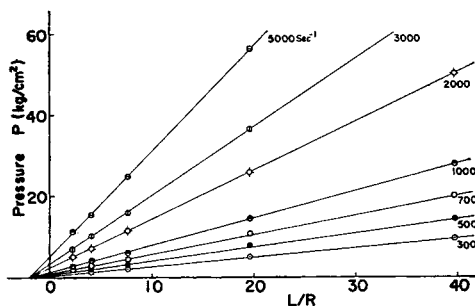


Fig. 2. Pressure P vs. capillary dimensions (L/R) of sodium silicate solution at 30°C.

where S_R is the recoverable shear strain at radius R . We can rearrange eq. (3) to obtain:

$$P_T = \tau_{cR}[(2L/R) + 2n + S_R] + m\rho V^2 \quad (6)$$

If we neglect the kinetic energy correction, eq. (6) can be written as:

$$P_T = \tau_{cR}[(2L/R) + 2n + S_R] \quad (7)$$

Equation (7) shows that P_T is linear function of L/R ; investigating P_T at a constant rate of shear for capillaries of different ratios of L/R , we can calculate τ_{cR} and $(n + S_R/2)$.

Figure 1 shows the relationship between pressure P_T and capillary dimensions L/R in 54.1 wt.-% solution of acrylonitrile copolymer of molecular weight 7.0×10^4 in NaCNS aqueous solution at 120°C. The Couette correction n can be obtained by the plots of pressure against capillary dimension in sodium silicate solution at a low shear stress (Fig. 2). In this case we could not find recoverable shear strain S_R ; 2.03 was obtained for the value of n .

The shear modulus of concentrated solutions of polymer can be calculated from the slope of the plot of recoverable shear strain against shear stress.

Apparatus and Material Used

The testing apparatus used in this work is a plunger extrusion rheometer produced by the Shimazu Seisakusho Co., Ltd., Japan. The L/R ratio

of capillaries used, which were drilled in cylinders of stainless steel, was varied from 2 to 30. All capillaries reported here had 180° entry angles.

All samples studied were acrylonitrile-methyl acrylate copolymer (90/10) prepared in a continuous reactor with a redox system as catalyst. The molecular weights of samples were 3.55×10^4 to 26.9×10^4 , as determined from intrinsic viscosity at 30°C . in dimethylformamide by using the equation:

$$[\eta] = 6.59 \times 10^{-4} \bar{M}_w^{0.66}$$

Reagent-grade sodium thiocyanate and deionized water were used in the preparation of polymer solution. Polymer solutions were prepared by mixing dried polymer and 55% NaCNS aqueous solution as solvent, and dissolving the polymer at 120°C . under pressure. The concentration range covered was 25–60% solids.

RESULTS

Figures 3–6 show the resultant plots of recoverable shear strain against shear stress for concentrated solutions of acrylonitrile copolymer having different molecular weights at various polymer concentrations. In the

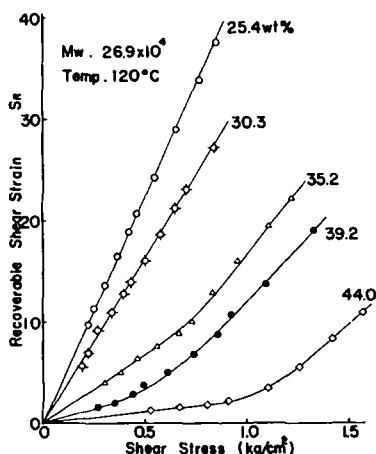


Fig. 3. Recoverable shear strain vs. shear stress plots for concentrated solution of acrylonitrile copolymer with $M_w 26.9 \times 10^4$ in various concentrations.

lower concentration range, the elastic behavior of the solutions of acrylonitrile copolymer follows Hooke's law up to critical concentration. Above a critical polymer concentration, the shear moduli (slopes of the plots of the recoverable shear strain versus the shear stress) depend on shear stress.

Figure 7 shows the plots of zero shear modulus G_0 (initial slope of the recoverable shear strain-shear stress relationship determined by capillary

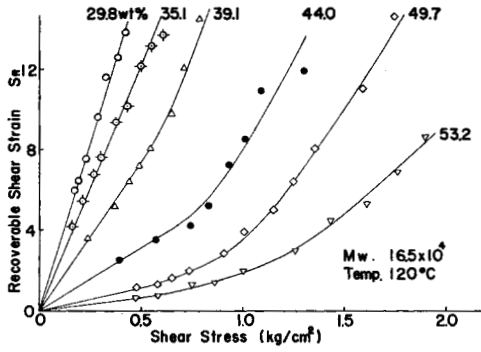


Fig. 4. Recoverable shear strain vs. shear stress plots for concentrated solution of acrylonitrile copolymer with $M_w 16.5 \times 10^4$ in various concentrations.

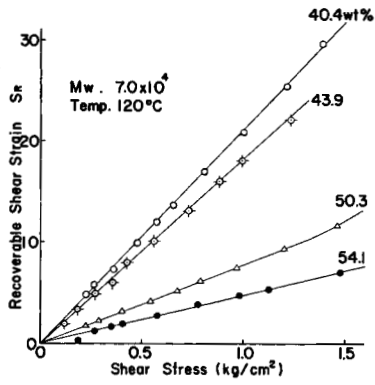


Fig. 5. Recoverable shear strain vs. shear stress plots for concentrated solution of acrylonitrile copolymer with $M_w 7.0 \times 10^4$ in various concentrations.

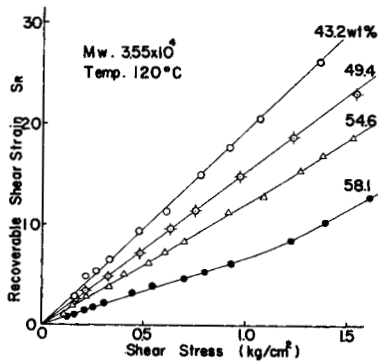


Fig. 6. Recoverable shear strain vs. shear stress plots for concentrated solution of acrylonitrile copolymer with $M_w 3.55 \times 10^4$ in various concentrations.

end correction method) against polymer concentration of acrylonitrile copolymers of various molecular weights.

The log-log plot of zero shear modulus against polymer concentration obviously falls on two straight lines with different slopes within experimental error. The intersection of the line is considered to be the onset of a long-range, elastically deformable entanglement network. If we call the inflection point of the logarithmic plot of zero shear modulus against polymer

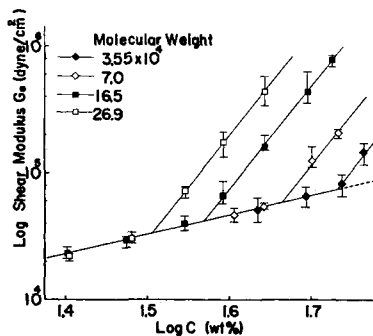


Fig. 7. Zero shear modulus vs. polymer concentration of acrylonitrile copolymer with various molecular weights.

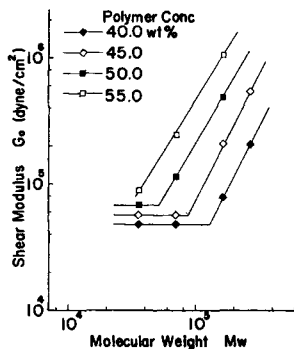


Fig. 8. Zero shear modulus vs. molecular weight of acrylonitrile copolymer at various concentrations.

concentration critical concentration $(C_c)_e$, the critical concentration $(C_c)_e$ decreases with increasing molecular weight. The slope of the plot of $\log G_0$ against $\log C$ changes abruptly from 1.5 to 8.0 at the critical polymer concentration $(C_c)_e$, regardless of molecular weight.

Moreover, up to the critical polymer concentration $(C_c)_e$, zero shear moduli of the concentrated solutions of acrylonitrile copolymer having different molecular weights are quite identical. This can be understood easily by referring to Figure 8, which is replotted from Figure 7. Figure 8 shows that zero shear modulus does not change with increasing molecular

weights up to the critical molecular weight (M_c)_e; the slope of the plots of $\log G_0$ against $\log M$ is 2 above the critical molecular weight (M_c)_e.

Figure 9 shows the plot of $\log \eta$ against $\log C$ at rates of shear of 100, 1000, and 10,000 sec.^{-1} . In this figure, we can not find the inflection point in the plot of $\log \eta$ against $\log C$ at the critical polymer concentration (C_c)_e; $\log \eta$ increases linearly with $\log C$. Viscosity η decreases with increasing rate of shear, even below the critical polymer concentration (C_c)_e. This fact indicates that shear modulus of concentrated solution of acrylonitrile copolymer is linear with shear stress below the critical polymer concentration (C_c)_e, but viscosity depends on rate of shear and shows the

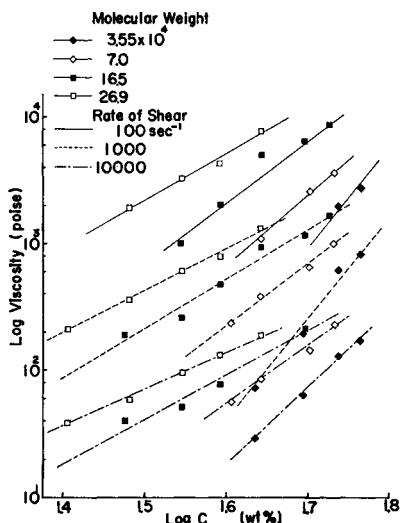


Fig. 9. Viscosity plotted against concentration of acrylonitrile copolymer with various molecular weight.

nonlinearity for rate of shear even below the critical polymer concentration (C_c)_e. The slope of the plot of $\log \eta$ against $\log C$ decreases with increasing rate of shear at the same molecular weight as already reported.⁸ The slope of the plot of $\log \eta$ against $\log C$ also decreases with increasing molecular weight at the same rate of shear.

DISCUSSION

It has been reported by many authors^{9,10} that the gel elasticity coefficient of gels is approximately proportional to the square of gel solids. At extremely high solids, the elasticity coefficient deviates from the square law and increases steeply (as high as some thousand times). The relationship between shear modulus and polymer concentration on the concentrated solutions of acrylonitrile copolymers is similar to that for the gel elasticity.

Thus, the elastic behavior of concentrated solutions of acrylonitrile copolymers seems to be based on the same network structure as that of gels.

The results obtained in this work are expressed by eqs. (8) and (9)

$$\begin{aligned} G_0 &\propto C^{1.5}M^0 \\ \eta &\propto C^\alpha M^\beta \end{aligned} \quad M < (M_e)_e, C < (C_e)_e \quad (8)$$

$$\begin{aligned} G_0 &\propto C^8 M^2 \\ \eta &\propto C^\alpha M^\beta \end{aligned} \quad M > (M_e)_e, C > (C_e)_e \quad (9)$$

where $\alpha = 4.83$ ($M_w = 16.4 \times 10^4$, rate of shear = 100 sec.⁻¹) and $\beta = 1.34$ ($C = 47.3\%$, rate of shear = 100 sec.⁻¹)

Hirai¹⁰ investigated the gel solids and gel molecular weight dependencies of the elastic coefficient of gels by using the kinetic theory of rubberlike elasticity. We applied this concept to the pseudo-network structure of concentrated solutions of acrylonitrile copolymers.

If ν_e is the number of effective crosslinkages in a unit volume made by chain entanglement in the concentrated solution, the shear modulus can be expressed by the relation,

$$G = \nu_e kT \quad (10)$$

where k is Boltzmann's constant and T is the absolute temperature. When the volume fraction of polymer in solution is v_2 , each molecule should be stretched by a factor of $v_2^{-1/3}$ in three directions and so shear modulus increases by the factor.

$$G = \nu_e kT v_2^{-1/3} \quad (11)$$

As it is difficult to calculate the exact value of ν_e , an approximate estimation was attempted here.

If the molecular volume of solvent is V_0 and the number of molecules of solvent and polymer per unit volume of concentrated solution are n_1 and n_2 , respectively, then we have

$$V_0(n_1 + n_2 p) = N_A \quad (12)$$

where N_A is Avogadro's number and p is the degree of polymerization. The probability P of forming chain entanglements in concentrated solution is given by

$$P = sZpn_2/(n_1 + pn_2) = sZv_2 \quad (13)$$

where Z is the coordination number of a polymer segment and s is the coefficient which expresses the efficiency of forming chain entanglements in concentrated solution when polymer segments come into contact with each other.

The number of crosslinkages contained in a molecule decrease with decreasing polymer concentration, and in dilute solution some molecules

may not have crosslinkages. These molecules do not contribute to the elasticity polymer solution, since their macro-Brownian movements cannot be prohibited. It can be assumed that a molecule must contain an average of r chain entanglements in order to contribute to the elasticity.

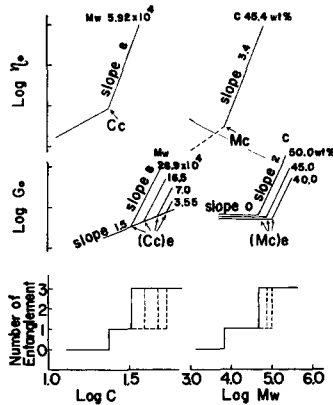


Fig. 10. Change of viscosity, shear modulus, and the number of chain entanglement with polymer concentration and molecular weight.

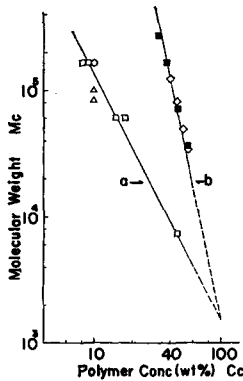


Fig. 11. Relationship between critical polymer concentration and critical molecular weight: (a) from viscosity measurement,⁸ (b) from elasticity measurement.

Then the total number of crosslinkages per unit volume of solution with an average of r chain entanglements per molecule can be calculated approximately by eq. (14):

$$\nu_e = \frac{1}{2} n_2 r (\hat{p} C_r) (s Z v_2)^r \doteq N_A Z^r p^{r-1} v_2^{r+1} S^r / 2(r-1)! V_0 \quad (14)$$

Thus we get the general formula for G from eq. (11),

$$G = R T Z^r p^{r-1} v_2^{r+2/3} s^r / 2(r-1)! V_0 \quad (15)$$

If we take $r = 1$ and $r = 3$ in eq. (15), we have

$$G \propto p^0 v_2^{1.67} \quad r = 1 \quad (16)$$

$$G \propto p^2 v_2^{3.67} \quad r = 3 \quad (17)$$

Thus, below the critical point, the shear modulus is expected to be proportional to the 1.67 power of polymer concentration and the zeroth power of molecular weight. As shown in eq. (8), the experimental results agree quite well with the prediction by the eq. (16). On the other hand, above the critical point, the shear modulus is expected to be proportional to the 3.67 power of polymer concentration and the square of molecular weight. Experimental results of molecular weight dependence of the shear modulus agree quite well with the expectation, but experimental results of polymer concentration dependence of the shear modulus disagree with the expectation by eq. (17). However, the parameter s which denotes the efficiency for forming chain entanglements when polymer segments come into contact with each other can be considered to change with polymer concentration especially above the critical point, that is to say, s is a function of v_2 , thus G may as well be proportional to more than the $(r + 2/3)$ th power of polymer concentration. Therefore, we know that the number of chain entanglement per molecule will change from one to three at the critical point $(C_c)_e$ or $(M_c)_e$.

When each molecule starts to form chain entanglements, the viscosity of the polymer solution increases rapidly. At the range of $C_c < C < (C_c)_e$ or $M_c < M < (M_c)_e$, the number of chain entanglement per molecule is kept one in polymer solution, however, at the range of $C > (C_c)_e$ or $M > (M_c)_e$, the number of chain entanglements per molecule increases to three. This relationship is shown schematically in Figure 10.

The value of $(C_c)_e$ or $(M_c)_e$ is shown in Tables I and II and Figure 11. Schreiber et al.⁴ reported that $(M_c)_e$ might be considerably greater than $2M_c$. In the present work, $(M_c)_e$ is greater than $6M_c$, and $(C_c)_e$ is greater than $2C_c$. As shown in Figure 11, $(M_c)_e/M_c$ decreases as polymer concentration increases, and $(C_c)_e/C_c$ decreases as molecular weight decreases; finally, $(C_c)_e$ and $(M_c)_e$ come to coincide with C_c and M_c , respectively, at 100% polymer concentration. This means that $(C_c)_e$ or $(M_c)_e$ exists only for polymer concentrated solutions but not for polymer melt.

TABLE I
Molecular Weight Dependence of $(C_c)_e$

Molecular weight $\times 10^4$	$(C_c)_e$, %	C_c , %*	$(C_c)_e/C_c$
3.55	53.9	20.2	2.67
7.0	46.2	13.8	3.35
16.5	37.1	8.7	4.27
26.9	32.1	6.65	4.83

* Data of Hayahara and Takao.⁸

TABLE II
Polymer Concentration Dependence of $(M_c)_e$

Polymer concentration, %	$(M_c)_e \times 10^{-4}$	$M_c \times 10^{-3a}$	$(M_c)_e/M_c$
40	12.4	10.0	12.4
45	8.1	7.8	10.4
50	4.9	6.5	7.5
55	3.4	5.4	6.3

^a Data of Hayahara and Takao.⁸

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Résumé

Le comportement élastique d'une solution concentrée d'un copolymère d'acrylonitrile a été étudié par la méthode de correction de l'extrémité du capillaire. On a obtenu les résultats suivants: Au-dessous d'une concentration critique, la tension de cisaillement est proportionnelle à la partie recouvrable du cisaillement, ceci est en accord avec la loi de Hooke. Au-dessus de la concentration critique, cependant, le module de cisaillement dépend de la tension de cisaillement. La relation entre le module de cisaillement à vitesse de cisaillement nulle et la concentration en polymère et le poids moléculaire suivant une échelle log-log tombe entre deux lignes droites de pente différente. L'intersection des lignes est considérée comme étant l'origine d'un réseau enchevêtré élastiquement déformable. Nous marquons le point d'inflexion par $(C_c)_e$ ou $(M_c)_e$. Le graphique de viscosité relatif à la concentration de polymères employés en échelle log-log ne montre pas le changement de pente à la concentration critique $(C_c)_e$. Par l'application de la théorie cinétique de l'élasticité caoutchouteuse au pseudo réseau d'une solution concentrée de polymère dans la gamme de $C_c < C < (C_c)_e$ ou $M_c < M < (M_c)_e$, le nombre d'entrelacements et par molécule est égal à un, dans la gamme de $C > (C_c)_e$ ou $M > (M_c)_e$, le nombre d'entrelacements augmente jusqu'à trois.

Zusammenfassung

Das elastische Verhalten einer konzentrierten Acrylnitrilcopolymerlösung wurde mit der Methode der Kapillarendenkorrektur untersucht. Folgende Ergebnisse wurden erhalten: (a) Unterhalb einer kritischen Konzentration ist, in Übereinstimmung mit dem Hooke'schen Gesetz die Schubspannung der reversiblen Schubverformung propor-

tional; oberhalb der kritischen Konzentration hängt dagegen der Schubmodul von der Schubspannung ab. (b) Das Diagramm des Moduls beim Schub Null gegen Polymerkonzentration und Molekulargewicht im doppelt logarithmischen Masstab besteht aus zwei geraden Linien mit verschiedener Neigung; der Schnittpunkt der Linien wird als charakteristisch für das Auftreten eines elastisch deformierbaren Verschlingungsnetzwerkes betrachtet. Der Wendepunkt wird mit $(C_c)_e$ oder $(M_c)_e$ bezeichnet. (c) Das Diagramm der Viskosität gegen die Polymerkonzentration im doppelt logarithmischen Masstab zeigt keine Neigungsänderung bei der kritischen Konzentration $(C_c)_e$. (d) Bei Anwendung der kinetischen Theorie der Kautschukelastizität auf die Pseudonetzwerkstruktur von konzentrierten Polymerlösungen ergibt sich im Bereiche $C_e < C < (C_c)_e$ oder $M_e < M < (M_c)_e$ die Zahl der Kettenverschlingungen pro Molekül zu eins; im Bereich $C > (C_c)_e$ oder $M > (M_c)_e$ steigt die Zahl der Kettenverschlingungen auf drei an.

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