

Viscoelastic Behavior of Partly Decrosslinked Polymer Networks. I. Acrylic Acid Anhydride-Crosslinked Poly(ethyl Acrylate)

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Synopsis

Acrylic acid anhydride (AAA) and tetraethylene glycol dimethacrylate (TEGDM) were employed as labile and permanent crosslinking monomers for poly(ethyl acrylate), respectively. Upon partial or total hydrolysis of the AAA crosslinks, various states of viscoelastic creep and stress relaxation were brought about. The use of chemically active monomers for crosslinking permits new polymer structures to be synthesized. In this case, decrosslinking converts a thermoset polymer into its thermoplastic counterpart. The relationship between the present decrosslinking study and a new nomenclature theory of grafted and crosslinked polymers is explored.

INTRODUCTION

The viscoelastic behavior of imperfectly crosslinked polymer networks is both of practical and theoretical interest. On the practical side, polymers both above and below their glass transition temperatures exhibit excessive creep and flow when undercured or degraded. Epoxy adhesives, for example, are sometimes not fully cured following application; raising the temperature while in service may then cause the adhesive to fail.^{1,2} Undercured elastomers also display excessive creep, as do materials that are subject to excessive heat.

The theoreticians have worried about polymerization and gelation kinetics,³ about dangling chain ends,⁴ and about molecular weights of chain segments between crosslinks.⁵ The study of polymer degradation also has a long history; for example, the stress relaxation behavior of degrading elastomers has yielded new insights into the chemistry of oxidative scission. Most of these studies involved random degradation; in this study (and the papers that follow), specific bonds will be selectively degraded to produce easily characterizable network changes.

THEORETICAL ASPECTS

In a series of theoretical papers, Sperling and co-workers have been developing nomenclature schemes for polymer blends, grafts, and interpenetrating polymer

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Fig. 1. Illustration of the use of ring theory to describe polymer blends, grafts, and crosslinked homopolymers. Upper left and right, ordinary addition and multiplication. Lower left and right, polymer blends, and grafted and crosslinked systems.

networks.⁶⁻⁸ Most recently, the mathematical ring-like characteristics of these materials were evolved.⁸ A formal ring has two operations, which in ordinary algebra are addition and multiplication (see Fig. 1). In the case of interest presently, nonbonded polymer blends serve as the addition mode, while grafted and crosslinked polymers serve as the multiplication mode, as also shown in Figure 1. Under binary operation o_2 , the combination

$$P_1 o_2 P_1 = C_1 \quad (1)$$

is found, where polymer 1 reacts with itself to yield the crosslinked product. Upon specifically removing the crosslink sites, the linear polymer 1 reappears. This procedure is the equivalent of transforming the element C_1 in the graft-crosslink table into its equivalent in the blends table, which, in this case, is just P_1 . (Note that coefficients which denote quantities of materials involved are omitted for simplicity.) A formal function, β , was evolved⁶ to describe the transformation:

$$\beta C_1 = \beta(P_1 o_2 P_1) = P_1 o_1 P_1 = P_1 \quad (2)$$

Concepts of this type have led to a search for degradation reactions specific to the crosslink sites. The best reaction found so far involves the use of anhydrides, which can be easily hydrolyzed.³

It can be argued that incompletely crosslinked polymer materials can be made by straightforward syntheses. Systematic lowering of the crosslink unit concentration will bring forth a range of viscoelastic properties. However, preparation of fully crosslinked networks followed by selective decrosslinking may allow certain properties to be emphasized, thus enhancing our understanding of their particular roles. Either the polymer can be partly crosslinked, or fully

TABLE I
Characterization of PEA Networks^a

	Sample no.						
	1	2	3	4	5	6	7
1-Doth, ml	0	0	0	0	0	0	0
AAA, ml	1.2	0.56	0.56	0.28	0	0	0
TEGDM, ml	0	0	1.4	0.70	2.9	1.4	0
$M_c(L) \times 10^4$	0.9	1.2	0.9	1.5	0.8	1.4	110
$M_c(Wg) \times 10^4$	1.2	1.7	0.9	1.6	0.7	1.5	90
$M_c(Th) \times 10^4$	1.0	2.0	1.0	2.0	1.0	2.0	∞
$M_c(E) \times 10^4$	0.9	1.2	0.9	1.3	0.7	1.2	1.7

^aEA, 100 ml; benzoin, 0.4 g.

TABLE II
PEA Networks with 0.68% 1-Dodecanethiol^a

	Sample no.						
	8	9	10	11	12	13	14
1-Doth, ml	0.68	0.68	0.68	0.68	0.68	0.68	0.68
AAA, ml	1.2	0.56	0.56	0.28	0	0	2.4
TEGDM, ml	0	0	1.4	0.7	2.9	1.4	0
$M_c(L) \times 10^4$	2.8	5.8	2.0	7.3	2.0	—	1.1
$M_c(Wg) \times 10^4$	2.6	4.6	2.4	6.6	2.1	—	1.2
$M_c(Th) \times 10^4$	1.9	3.9	2.0	4.0	2.0	4.1	1.0
$M_c(E) \times 10^4$	0.8	1.2	0.9	1.4	0.8	1.2	0.6
		After Hydrolysis (NH ₄ OH)					
$M_c(L) \times 10^4$	3.6	7.8	3.5	8.6	2.2	—	—
$M_c(Wg) \times 10^4$	4.8	7.5	3.1	7.3	2.0	—	—
$M_c(E) \times 10^4$	1.2	2.1	1.0	2.1	0.8	1.0	1.3

^aEA; 100 ml; benzoin, 0.4 g.

crosslinked and then partly decrosslinked, to arrive at the same nominal point. However the structures, and hence their viscoelastic behavior, may differ.

The reader will note that while the ring theory suggests selective crosslink site attack, and presumes it complete, the incomplete reaction stage has much greater interest to the students of viscoelasticity.

EXPERIMENTAL

The photochemical method of synthesizing poly(ethyl acrylate) (PEA) networks in bulk with UV light has been previously described.⁹ In brief, benzoin was used as the initiator, acrylic acid anhydride (AAA) was used as the labile crosslinker, and tetraethylene glycol dimethacrylate (TEGDM) was used as the permanent crosslinker. The chemical 1-dodecanethiol (1-Doth) was employed as a chain transfer agent. This last was necessary because side reactions during the polymerization of ethyl acrylate lead to gelation even without added crosslinker. The exact levels of TEGDM, AAA, and 1-Doth employed are shown in Tables I–III.

Decrosslinking studies were done using ethylenediamine and ammonium hydroxide. In another paper,⁸ it was found that ethylenediamine was effective

TABLE III
 PEA Networks Capable of Complete Hydrolysis^a

	Sample no.					
	15	16	17	18	19	20
1-Doth, ml	1.36	1.36	1.36	1.36	1.36	2.7
AAA, ml	1.2	0.56	0.56	0.28	2.4	2.4
TEGDM, ml	0	0	1.4	0.7	0	0
$M_c(L) \times 10^5$	1.6	3.5	0.36	4.3	1.0	0.75
$M_c(Wg) \times 10^5$	1.6	3.6	0.37	3.8	0.7	0.54
$M_c(E) \times 10^4$	1.4	2.0	1.2	3.0	0.75	0.78
After Hydrolysis (NH ₄ OH)						
$M_c(L) \times 10^5$	sol	sol	0.47	5.3	sol	sol
$M_c(Wg) \times 10^5$	sol	sol	0.44	5.0	sol	sol
$M_c(E) \times 10^5$	3.5	5.2	0.36	2.6	1.6	1.6

^aEA, 100 ml; benzoin, 0.4 g.

in decrosslinking polystyrene networks; however, soaking the PEA for 24 hr in 28% NH₄OH was very effective, and this reagent was adopted for the present study.

The materials were characterized before and after hydrolysis by swelling them for one day in methyl ethyl ketone (MEK). Both the weight increase and the changes in length were recorded.

The creep properties were investigated using Gehman^{10,11} and Clash-Berg¹² type creep testers; also tensile creep studies were performed.

RESULTS

Values of M_c , the molecular weight between crosslink sites, obtained by swelling the samples in MEK were calculated by the Flory-Rehner equation:^{13,14}

$$\frac{1}{M_c} = \frac{\ln(1 - v_2) + v_2 + \chi_{12}v_2^2}{\rho V_0[v_2^{1/3} - (v_2/2)]} \quad (3)$$

where v_2 represents the volume fraction of polymer in the sample at equilibrium; V_0 is the solvent molar volume, of density ρ ; and the value of the interaction parameter χ_{12} was taken to be 0.46, which is the value for PEA in acetone.¹⁵ While the value of χ for PEA in MEK has not been determined, the equilibrium swelling values of crosslinked PEA in acetone and MEK were determined on one sample and found to be nearly the same. Thus, χ for PEA in MEK was taken to be the same as in acetone.

In each case, volumes were assumed to be additive. Values reported in Tables I-III were based on actual weight gain, $M_c(Wg)$, and on length change, $M_c(L)$. In addition, values were estimated from Young's modulus E via the theory of rubber elasticity, $M_c(E)$:

$$M_c(E) = \frac{3\rho RT}{E} \quad (4)$$

By way of characterization, the density of several samples was measured by pycnometer, and was found to vary from 1.10 to 1.19 g/cm³, depending on the

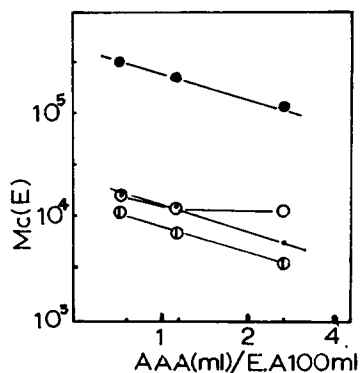


Fig. 2. Values of $M_c(E)$ as a function of AAA and 1-Doth levels, before and after hydrolysis: (○) 0.68% 1-Doth before hydrolysis; (○) 0.68% 1-Doth after hydrolysis; (●) 1.3% 1-Doth before hydrolysis; (●) 1.3% 1-Doth after hydrolysis.

crosslink level. During the swelling tests, only 1–2% of material was extracted, indicating reasonably crosslinked products.

Values of M_c via both swelling and modulus are compared to the theoretical values, $M_c(Th)$, calculated on the basis of actual amounts of crosslinker added, assuming infinite primary chain length. Experimental values of M_c are shown to agree with theory in Table I, except for the far right-hand column. With no added crosslinks, a value of M_c equal to the molecular weight itself is expected, but since infinite chains were assumed in the $M_c(Th)$ calculations, a value of ∞ is reported for the case of no crosslinks. Finite values are noted experimentally, with much smaller values obtained via the modulus [$M_c(E)$] experiment. This last is because physical entanglements count effectively as crosslinks. The values of $M_c(L)$ and $M_c(Wg)$ of sample 7, without any crosslinking agent added, is seen to be much larger than samples 1–6. However, $M_c(E)$ for sample 7 is only slightly larger, the value for E being 5.1×10^6 dynes/cm² at 25°C. This is due to the method of measurement, since Young's modulus E measures physical entanglements as well as actual chemical crosslinks.

In general, the relative effect of the physical entanglements increase in importance as the density of chemical crosslinks decreases. For example, comparison of samples 4, 11, and 18 shows $M_c(Wg)$ increasing faster than $M_c(E)$ as more 1-Doth is added. None of the materials shown in Table I would dissolve after hydrolysis, although increased swelling values were noted.

In an attempt to counteract the accidental gelation reactions, various quantities of 1-dodecanethiol were introduced to promote chain transfer reactions. As shown in Tables II and III, at a level of 1.36% 1-Doth or greater, the polymers are soluble after hydrolysis. Using 1-Doth causes $M_c(L)$ and $M_c(Wg)$ of all samples to increase (reduced crosslinking), as illustrated in Tables II and III. After hydrolysis, the $M_c(L)$, $M_c(Wg)$, and $M_c(E)$ values of samples only containing TEGDM are not changed, but samples containing AAA are increased. The result is clear: the effect of 1-Doth is to cut the main chains during synthesis, but the ammonium hydroxide only attacks the AAA crosslink site. The values of $M_c(E)$ on the bottom row of Table III represent the limiting level of physical crosslinks only.

To summarize the effects of AAA on $M_c(E)$, values are plotted in Figure 2

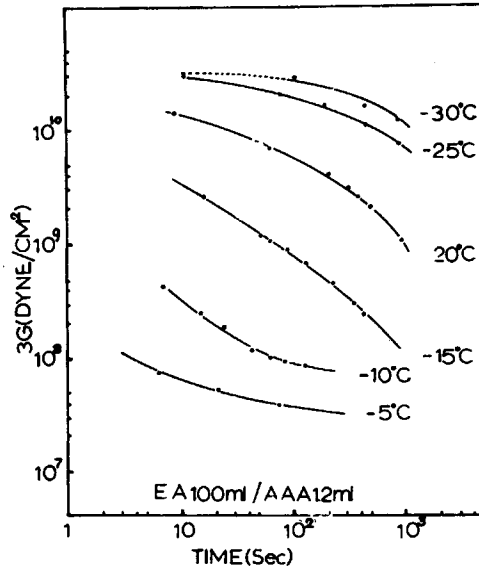


Fig. 3. Values of $\log 3G$ vs time in the glass transition temperature range of PEA.

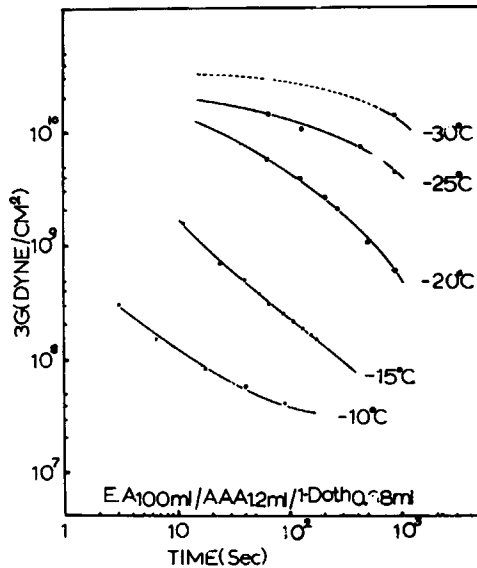


Fig. 4. Values of $\log 3G$ vs time for a series of temperatures for a material containing 0.68% 1-Doth.

before and after hydrolysis for two different 1-Doth levels. (Note that a decreasing M_c value indicates an increased crosslinking level.)

As a last step in characterizing the PEA networks, a simple Gehman-type creep test is shown in Figure 3 for PEA containing 1.2% AAA, before hydrolysis. The reported T_g of this material, -22°C , agrees well with the result, and a well-defined rubber plateau is approached at -5°C . Addition of 0.68% of 1-Doth increases the rate of creep somewhat, as shown in Figure 4. After hydrolysis, the

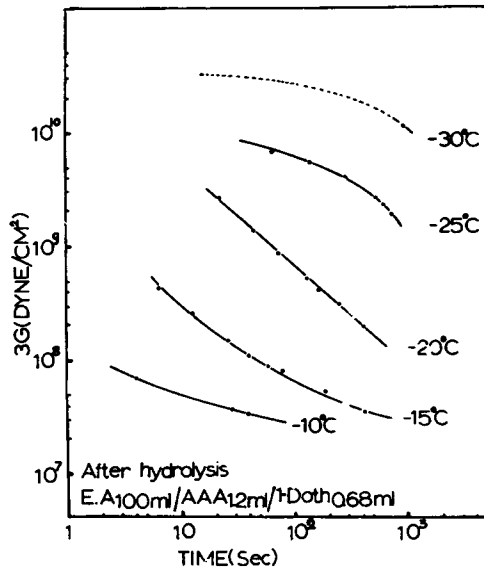


Fig. 5. Values of $\log 3G$ vs temperature for PEA, after hydrolysis, for a PEA containing 1.2 ml AAA and 0.68% 1-Doth.

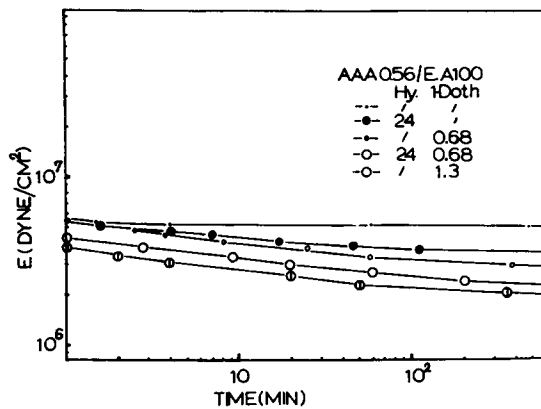


Fig. 6. Stress relaxation of PEA networks before and after hydrolysis.

rate of creep was increased still more, as shown in Figure 5. The creep rate of samples which contained only TEGDM and not any AAA was not appreciably changed after hydrolysis. The creep rates of samples containing both TEGDM and AAA was increased after hydrolysis (data not shown), but the magnitude of the change was not as large as is shown in Figures 4 and 5, which represents the limiting case of only AAA. Even though viscoelasticity increases from Figure 3 to Figure 5, the actual glass transition temperature probably remains nearly the same, only the molecular weight distributions in relation to the crosslink levels were changed.

Stress relaxation studies on a series of networks are shown in Figures 6 and 7. The modulus E was calculated from

$$\frac{w \times 981}{A} = \frac{E}{3} \left(\alpha - \frac{1}{\alpha^2} \right) \quad (5)$$

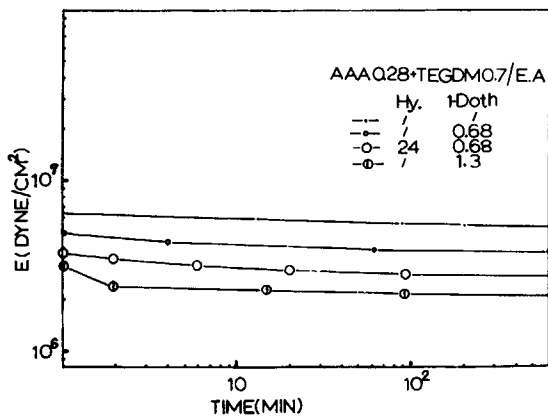


Fig. 7. Stress relaxation of PEA networks containing both permanent and temporary crosslinks sites.

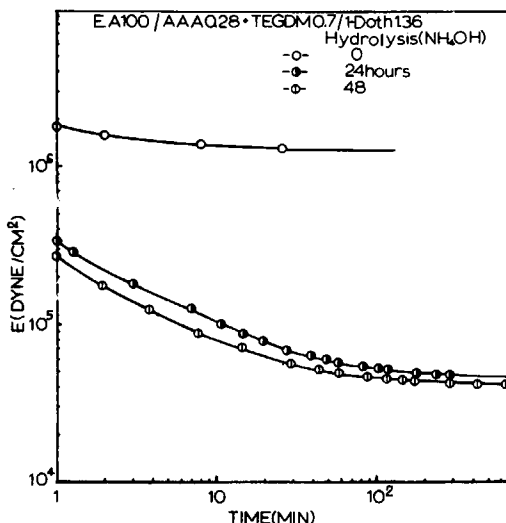


Fig. 8. Stress relaxation of PEA networks as a function of hydrolysis time.

where w equals the weight applied, A is the cross-sectional area of the sample, and α is the elongation, equal to the final length over the initial length. For high elongations, the engineering strain, $2\alpha^2 + (1/\alpha)$, was employed for modulus calculations. In each of the materials shown in Figures 6 and 7, the network remained intact after hydrolysis, although at a lower level of crosslinking.

The effect of hydrolysis time is shown in Figure 8. The level of 1-Doth, 1.36%, permits solubility after hydrolysis, as noted in Tables II and III. The TEGDM employed, however, kept the networks intact. Note that only a small effect is noted on the behavior between 24 and 48 hr of hydrolysis time.

The tensile creep modulus of several networks is shown in Figure 9. At a level of 1.36% 1-Doth, the network structures of the materials without TEGDM are seen to be completely destroyed. Creep was rapid enough to cause sample failure after only a few minutes. However, samples having TEGDM only behave as if the crosslink level remains unchanged. Figure 9 shows that only the AAA part

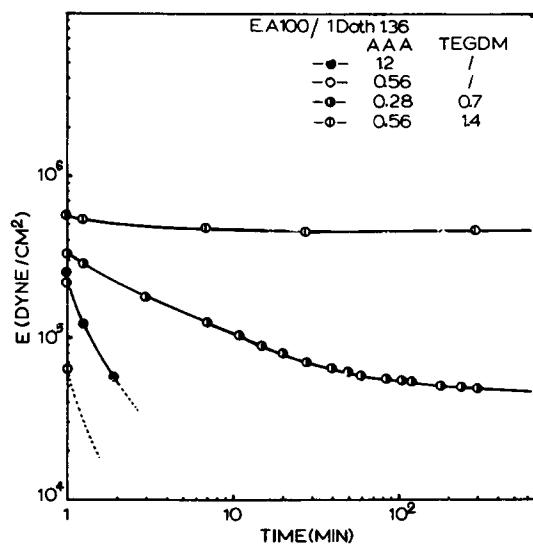


Fig. 9. Tensile creep modulus of several PEA samples, after hydrolysis, for 24 hr at 25°C.

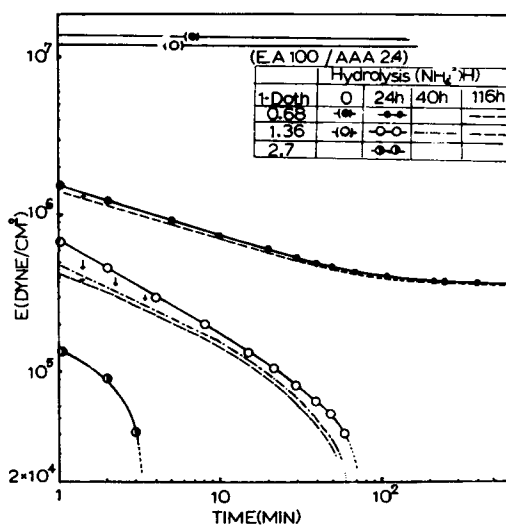


Fig. 10. Creep modulus of samples having little or no network properties after hydrolysis for 24 hr at 25°C in 28% Na_4OH .

of samples containing both AAA and TEGDM is broken by the ammonium hydroxide. After hydrolysis, the crosslink density depends on the TEGDM level, as shown in Table III and Figure 9.

While Figures 8–10 show creep behavior in the rubber and rubbery flow temperature regions of the samples, Figures 3–5 show the equivalent data in the glassy and glass transition region.

Finally, Figure 10 summarizes the creep modulus behavior of hydrolyzed samples having various levels of 1-Doth. At 0.68% 1-Doth, a network is retained, and the modulus does reach a plateau. At 1.36% 1-Doth, the polymer is just soluble, and failure occurred after about 1 hr. At 2.7% 1-Doth, creep is much

more rapid, due undoubtedly to the lower molecular weight remaining, and the sample failed after only a few minutes.

DISCUSSION AND CONCLUSIONS

In this first paper on selective decrosslinking and degrafting, the behavior of acrylic acid anhydride crosslinked poly(ethyl acrylate) was explored. Figure 1 shows four tables in summary form. The top two show the ordinary arithmetic operations of addition and multiplication. The bottom two tables show the equivalent operations of blending and crosslinking or grafting. While the analogy is obviously inexact, it provides a basis for many combinations and transformations. Through use of these tables, arbitrarily complex materials can be conceived and named and their relationship to other materials described. The decrosslinking reaction described herein is one of the simplest transformations possible. Equation (2) described the ring theory transformation from a crosslinked polymer to a linear polymer with the use of the β function. In this case, the specific degradation of the crosslink sites themselves, rather than a random-type degradation, is specified. The simple case of total decrosslinking has already been briefly explored.⁸ The more interesting case from a viscoelastic point of view involves selective partial decrosslinking.

Hydrolysis of AAA can be effected by ethylenediamine,⁸ sodium hydroxide in water, or ammonium hydroxide in water. For PEA crosslinked with AAA, the hydrolysis of the AAA was found to be substantially complete after 24 hr of soaking with 28% ammonium hydroxide solutions, making this a practical reagent for PEA/AAA systems.

Even after hydrolysis, the samples containing only AAA but also only modest amounts of 1-Doth did not flow. These samples apparently had some remaining gelation, due to the side reactions during synthesis. Note that the materials in Figures 2 and 10, which should have flowed in the absence of side reactions, in fact did not.

Thus, without a sufficient amount of chain transfer agent (1-Doth), side reactions which normally occur in the free-radical polymerization of PEA created a gelled sample even in the absence of deliberately introduced crosslinking agents. With 1-Doth present, a branched polymer must be present because 1-Doth does not suppress the side reactions; it only causes the chains to be cut at random points.

By controlling the AAA and 1-Doth levels, materials just at the critical gel point were created. These materials exhibited low moduli and large creep values.

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