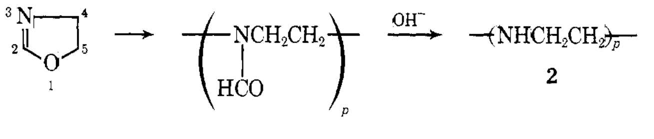
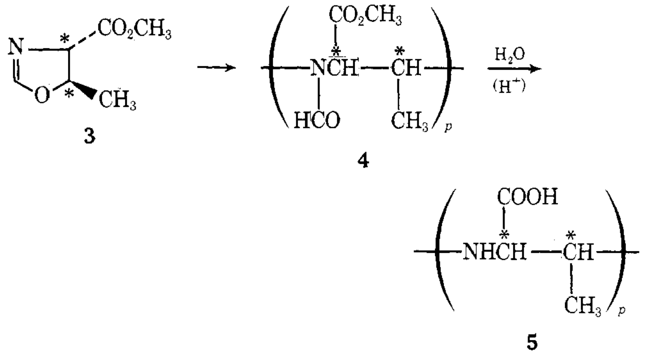
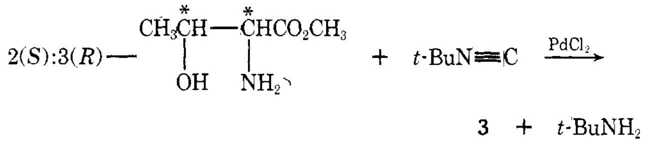
Communications to the Editor

Polymerization of (4*S*,5*R*)-4-Carbomethoxy-5-methyl-2-oxazoline

Cationic polymerization of unsubstituted 2-oxalzoline was first realized by us to produce poly(*N*-formylethylenimine) (**1**), which was converted by hydrolysis into linear poly(ethylenimine) (**2**). This is a useful process for the preparation of nonbranched poly(ethylenimine). On the basis of this method, optically active polymers having well-defined structures are prepared from the corresponding optically active 2-oxazolines having a substituent at the 4 or(and) 5 position. A previous paper[1] of ours reported the polymerization of 4(*S*)-4-methyl-2-oxazoline followed by the hydrolysis of the polymer to produce optically active poly(propylenimine). Here, we wish to report a new optically active polymer of the poly(ethylenimine) family, containing a carboxyl group. The monomer, (4*S*,5*R*)-4-carbomethoxy-5-methyl-2-oxazoline (**3**) ($[\alpha]^{13}\text{D}$ 231°; THF solution, *c* 0.375), was prepared by a new method we have developed, in which methyl 2(*S*):3(*R*)-threonate ($[\alpha]^{13}\text{D}$ +3.4°) was reacted with *tert*-butyl isocyanide in the presence of $PdCl_2$ as catalyst.[2]







$$2(S){:}3(R)\text{—}\underset{\text{OH}}{\text{CH}_3\overset{*}{\text{C}}\text{H}}\text{—}\underset{\text{NH}_2}{\overset{*}{\text{C}}\text{HCO}_2\text{CH}_3} + t\text{-BuN}{\equiv}\text{C} \xrightarrow{\text{PdCl}_2} 3 + t\text{-BuNH}_2$$

The polymerization of **3** was accomplished with cationic initiators such as CH_3I or CF_3SO_3Et in dimethylformamide at 100° for 120 hr. The reaction mixture was diluted with methanol and poured into excess ether. The precipitated polymer **4** was a light-brown solid (yield 60%, mp 186°). The molecular weight of **4** was found to be 1.34×10^3 by vapor pressure osmometry (DMF solution, Hitachi Perkin-Elmer 115). The polymer structure was established by elemental analysis and spectral data: pmr (DMSO-d_6) δ 1.2 (d, 3 H), 3.2 ~ 3.6 (m, 2 H), 3.8 (s, 3 H), 8.2 (s, 1 H); ir (KBr) 1740, 1665, 1610, 1510 cm^{-1}. *Anal.* Calcd for $C_6H_9NO_3$: C, 50.34; H, 6.34; N, 9.79. Found: C, 50.26; H, 6.31; N, 9.57. The specific rotation of **4** was $[\alpha]^{20}\text{D}$ −11° (MeOH solution, *c* 0.16) and the ORD spectrum exhibited a positive cotton effect near 253 nm.

The mechanistic study of the cationic polymerization of 2-unsubstituted-2-oxazoline established an SN2 mechanism between the propagating species of the oxazolinium ion and monomeric oxazoline.[3] Therefore, the polymerization of **3** is considered to proceed with inversion of configuration at carbon-5 (C-5) of monomer **3**. On the other hand, the stereochemistry of carbon-4 (C-4) bearing the carbomethoxy group should be intact since carbon-4 of monomer should not be involved in the propagation step.

Acid hydrolysis of the polymer **4** was carried out in aqueous HCl solution at 100° for 10 hr, giving rise to the HCl salt of **5**, as a hygroscopic solid polymer. The pmr spectrum of **5** revealed that signals which are ascribed to >NCHO and $-COOCH_3$ had disappeared completely. (HCl salt of **5**: pmr (D_2O) δ 1.2 (d, 3 H), 3.8 ~ 4.4 (m, 2 H); ir (KBr) 1730 cm^{-1}). The specific rotation of the HCl salt of **5** was $[\alpha]^{20}\text{D}$ +69° (MeOH solution, *c* 0.055).

References and Notes

(1) T. Saegusa, S. Kobayashi, and M. Ishiguro, *Macromolecules*, in press.
(2) Y. Ito, I. Ito, T. Hirao, and T. Saegusa, *Synth. Commun.*, **4**, 97 (1974).
(3) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 359 (1972); **6**, 315 (1973); T. Saegusa and H. Ikeda, *ibid.*, **6**, 868 (1973).

Takeo Saegusa,* Toshikazu Hirao, and Yoshihiko Ito
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto Japan 606

Received October 2, 1974

Entanglement Networks of 1,2-Polybutadiene Cross-Linked in States of Strain. II. Application of the Mooney–Rivlin Equation to Networks Cross-Linked at 0°

This paper gives the results of a recalculation of the data in paper I[1] of this series, with an expression for strain energy which is a special case of the Mooney–Rivlin theory, instead of the ideal theory based on Gaussian networks.

It was shown in paper I that the apparent concentration of elastically effective network strands terminated by entanglements, ν_N, can be estimated by cross-linking linear polymers in states of strain. The maximum value of ν_N found by this method was about one-half the value obtained from viscoelastic measurements in the rubbery plateau zone, $\nu_e = 2.5 \times 10^{-4}$ mol cm^{-3}. The low value of ν_N was primarily attributed to the cross-linking temperature being too far (12°) above the glass-transition temperature, T_g. Cross-linking temperatures closer to T_g give values of ν_N close to ν_e as will be shown in paper III[2] of this series. In addition, it was found that these networks behave slightly differently from the predictions of the ideal Gaussian composite network theory:[3] ideal Gaussian composite networks are isotropic relative to the state of ease whereas these networks exhibit anistropy of equilibrium swelling relative to the state of ease, in *n*-heptane; and ν_N, instead of being a constant, was found to decrease with increasing extension ratio during cross-linking, λ_0. The latter result is illustrated in Figure 1 for irradiation times from 3 to 5 hr; here, ν_N is plotted against the extension ratio, λ_s, in the state of ease in which the retractive force of the entanglement network and the compressive force of the cross-link network are equal and opposite in direction. The experimental points can be fitted rather well by a curve (not the one shown)

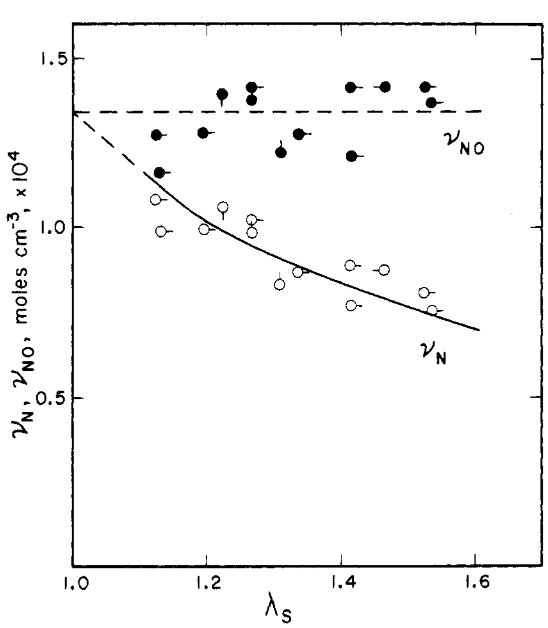


Figure 1. Concentration of elastically effective strands terminated by entanglements plotted against extension ratio in the state of ease, λ_s, for different irradiation times in hours. Pip up, 3.0; right, 4.0; down, 4.5; left, 5.0. Open circles, ν_N calculated from ideal Gaussian network behavior; filled circles, ν_{NO} calculated from Mooney-Rivlin treatment with $C_{1N} = C_{2x} = 0$.

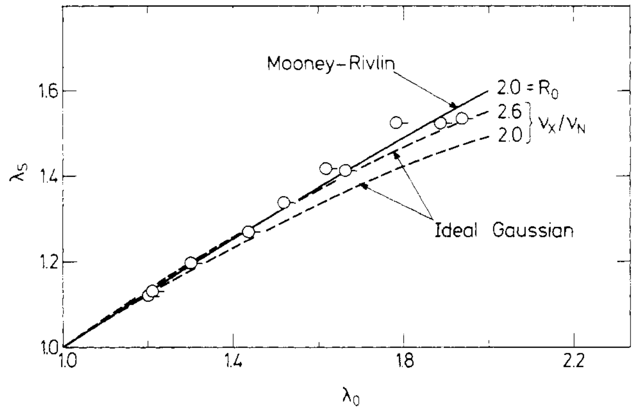


Figure 2. Extension ratio, λ_s, at state of ease plotted against extension ratio, λ_0, during irradiation for 4-hr irradiations at 0°. The solid line shows Mooney-Rivlin behavior while the two dashed lines show ideal Gaussian behavior.

with the functional form of a constant divided by λ_s, like the C_2 term in the Mooney-Rivlin equation.[4]

Although there have been objections[5] of a more fundamental nature to the use of the Mooney stored energy function for the case of simple elongation, we felt that it would be interesting to take the data of paper I and perform an analysis based on the Mooney function in an attempt to describe the observed deviations from ideal Gaussian composite network theory.

Application of the Mooney-Rivlin equation to composite networks which were cross-linked in both the isotropic and strained states has been tried by Greene, Smith, and Ciferri[6] who in their analysis retained all four constants in eq 1 for the elastic free energy, ΔF_{el}

$$\Delta F_{el} = C_{1N}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + C_{2N}(\lambda_x^{-2} + \lambda_y^{-2} + \lambda_z^{-2} - 3) + C_{1x}(\lambda_{x;2}^2 + \lambda_{y;2}^2 + \lambda_{z;2}^2 - 3) + C_{2x}(\lambda_{x;2}^{-2} + \lambda_{y;2}^{-2} + \lambda_{z;2}^{-2} - 3) \quad (1)$$

where in our notation C_{1N} is the C_1 constant and C_{2N} is the C_2 constant of the entanglement network while C_{1x} and C_{2x} are the corresponding constants for the cross-link network; λ_x, λ_y, and λ_z are the extension ratios relative to the original isotropic state; and $\lambda_{x;2}$, $\lambda_{y;2}$, and $\lambda_{z;2}$ are the extension ratios relative to the dimensions during cross-linking given by λ_{0x}, λ_{0y}, and λ_{0z}.

Now, recent studies of stress relaxation at large strains of uncross-linked polyisobutylene[7] suggest that the transient force divided by the term $(\lambda - \lambda^{-2})$ in the network of untrapped entanglements is nearly proportional to $1/\lambda$, *i.e.*, $C_2 \gg C_1$, whereas for cross-linked butyl rubber (and cross-linked rubbers in general) $C_2 < C_1$. These results suggest setting $C_{1N} = C_{2x} = 0$ so that eq 1 becomes

$$\Delta F_{el} = C_{2N}(\lambda_x^{-2} + \lambda_y^{-2} + \lambda_z^{-2} - 3) + C_{1x}(\lambda_x^2\lambda_{0x}^{-2} + \lambda_y^2\lambda_{0y}^{-2} + \lambda_z^2\lambda_{0z}^{-2} - 3) \quad (2)$$

(Another possible justification for setting $C_{2x} = 0$ is that the cross-link network is in compression in the state of ease, and C_2 from measurements of single networks in compression is even smaller than from measurements in tension.[5]) The derivation from eq 2 will be given in more detail in paper III.[2] Some of the results are as follows.

States of ease, in which ΔF is at a minimum, are given by the following equation

$$\lambda_0^3 - [(\lambda_s^3 - 1)/R_0\lambda_s]\lambda_0^2 - \lambda_s^3 = 0 \quad (3)$$

where $R_0 = C_{1x}/C_{2N}$. Figure 2 shows λ_s plotted against λ_0 for 4-hr irradiations. The solid line is plotted according to eq 3, above, with $R_0 = 2$, and it can be seen that this line is steeper, and gives a better fit to the data, than the dashed curves which are plotted according to eq 3 of paper I (ideal Gaussian composite network theory).

Young's modulus in the state of ease in the direction parallel to the stretching direction during irradiation, $(E_s)_\parallel$, is given by the following equation

$$(E_s)_\parallel = 6C_{2N}[\lambda_s^{-2} + (R_0/3)(\lambda_s^2\lambda_0^{-2} + 2\lambda_0\lambda_s^{-1}) \quad (4)$$

which in the range covered in these experiments is a monotonically decreasing function of λ_0 contrary to ideal Gaussian composite network theory which gives a monotonically increasing function as given in Figure 4 of paper I. The data points are unfortunately too scattered to confirm either of the two functions. Young's modulus perpendicular to the stretch direction, $(E_s)_\perp$, is found to be larger than $(E_s)_\parallel$ in agreement with the observed swelling anisotropy, but the analytical expression is too complicated to be included here. (An alternative interpretation to the observed anisotropy has been proposed by Smith and Gaylord.[8])

Identifying C_{2N} and C_{1x} with $\nu_{NO}RT/2$ and $\nu_xRT/2$, respectively, the constants ν_{NO} and ν_x can be calculated from eq 3 and 4 when λ_0, λ_s, and $(E_s)_\parallel$ are known from experiment. The subscript on ν_{NO} distinguishes it from ν_N calculated from eq 2 and 3 of paper I (ideal Gaussian composite network theory). In Figure 1, values of ν_{NO} calculated in this manner are also shown. In contrast to the sharp decrease in ν_N with increasing stretch ratio, ν_{NO} remains constant within experimental scatter. Other examples of the application of the Mooney-Rivlin theory to networks cross-linked at lower temperatures will be given subsequently.[2]

The method of cross-linking entanglement networks in strained states thus seems to be very promising for the study of the elastic effects of entanglements. If the Mooney-Rivlin treatment proves as successful in further tests which we are planning, including equilibrium swelling, this method might finally resolve the question concerning the molecular origin of the empirical C_2 term in the Mooney–Rivlin equation.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation and the ARPA Materials Research Council Contract No. DAHC 15-71-C-0253 with the University of Michigan.

References and Notes

(1) O. Kramer, R. L. Carpenter, V. Ty, and J. D. Ferry, *Macromolecules*, **7**, 79 (1974).

(2) O. Kramer, R. L. Carpenter, and J. D. Ferry, in preparation.

(3) P. J. Flory, *Trans. Faraday Soc.*, **56**, 722 (1960).

(4) L. R. G. Treloar, "The Physics of Rubberlike Elasticity," 2nd ed, Oxford University, Oxford, 1958, p 165.

(5) L. R. G. Treloar, *Rep. Progr. Phys.*, **36**, 755 (1973).

(6) A. Greene, K. J. Smith, Jr., and A. Ciferri, *Trans. Faraday Soc.*, **61**, 2772 (1965).

(7) C. R. Taylor, R. Greco, O. Kramer, and J. D. Ferry, unpublished experiments.

(8) K. J. Smith and R. J. Gaylord, preceding paper.

Ole Kramer
Chemistry Laboratory III
The University of Copenhagen
2100 Copenhagen ϕ, Denmark

John D. Ferry*
Department of Chemistry and Rheology Research Center
University of Wisconsin
Madison, Wisconsin 53706

Received September 24, 1974

On the Anisotropy of Composite Networks

Recently the elastic behavior of some specially prepared polymer networks was reported by Kramer, *et al.*[1] These networks, cross-linked in states of strain just above the glass transition temperature, were analogous to composite networks[2] in that an entanglement structure provided a stress level during cross-linking; the entanglements served as first stage cross-links.

These networks, prepared from polybutadiene, were mechanically anisotropic, with a lower modulus along the initial direction of stretch than in the transverse direction. Such anisotropy is in the opposite sense to that previously reported for true composites of rubber,[3] where the modulus along the transverse direction is lower. The theory of composites, based on Gaussian chains, cannot account for such anisotropic behavior.[2,4–6]

We wish to point out, however, that composite theory derived from non-Gaussian statistics does predict anisotropic elastic behavior.[7,8] One such model,[8] a composite network composed of a most probable chain contour length distribution of non-Gaussian chains undergoing an affine deformation, is in qualitative agreement with the experimental results of Kramer, *et al.*[1] Therefore, to the extent that entanglement–cross-link composites are comparable to cross-link–cross-link composites, we view their data as being an experimental validation of our theoretical results.[8] Since the theoretical anisotropy arises from the use of the most probable contour length distribution, a monodisperse system being isotropic, it is suggested that chain length distributions can have important bearings on the mechanical behavior of elastomers. The data reported by Kramer, *et al.*,[1] tend to add substance to this conclusion.

References and Notes

(1) O. Kramer, R. L. Carpenter, V. Ty, and J. D. Ferry, *Macromolecules*, **7**, 79 (1974).

(2) R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl. Phys.*, **17**, 352 (1946).

(3) A. Greene, K. J. Smith, Jr., and A. Ciferri, *Trans. Faraday Soc.*, **61**, 2772 (1965).

(4) J. P. Berry, J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **52**, 1137 (1956).

(5) P. J. Flory, *Trans. Faraday Soc.*, **56**, 722 (1960).

(6) A. S. Lodge, *Kolloid Z.*, **171**, 46 (1960).

(7) K. J. Smith, Jr., A. Ciferri, and J. J. Hermans, *J. Polym. Sci., Part A*, **2**, 1025 (1964).

(8) K. J. Smith, Jr., and R. J. Gaylord, *J. Polym. Sci., Part A-2*, **10**, 283 (1972).

K. J. Smith, Jr.*
Department of Chemistry
College of Environmental Science and Forestry
Syracuse, New York

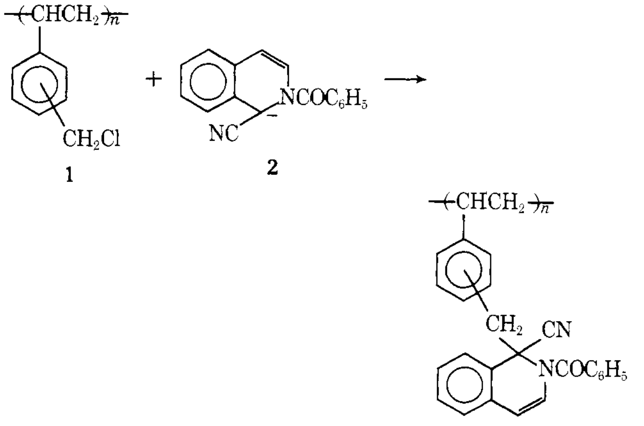
R. J. Gaylord
Department of Metallurgy and Mining Engineering
University of Illinois at Urbana-Champaign
Urbana, Illinois

Received July 22, 1974

Chemical Modification of Polymers. IV. Another Example of Facile Nucleophilic Attack on a Polymer by a Reissert Anion

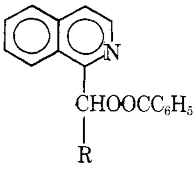
Recent progress in the field of chemical reactions of polymers[1,2] brought to our attention the opportunities for controlled alteration of chemical and physical properties of polymers. Our studies[3–5] have concentrated on polymeric reactions in solution. This allows more facile and complete analysis of the reaction process and products, while at the same time affording polymers of potentially greater utility than insoluble polymers.

In the previous report in this series the reaction of Reissert compounds and polymers bearing displacable halogens was examined and shown to be an excellent means of attaching aza-aromatic moieties to polymers.[5] Specifically, poly(vinylbenzyl chloride) (1) was reacted with the anion (2) of 2-benzoyl-1,2-dihydroisoquinaldonitrile. Displacement of chloride ion occurs, resulting in formation of poly[1-(vinylbenzyl)-2-benzoyl-1,2-dihydroisoquinaldonitrile] (3).



1 2 3

Other reactions of Reissert compounds[6] seem to be adaptable to grafting reactions of polymers. Among these is the reaction of aldehydes. The Reissert anion **2**, for instance, reacts with aldehydes (RCHO) to produce ester **4**



4

via an intramolecular rearrangement with loss of cyanide