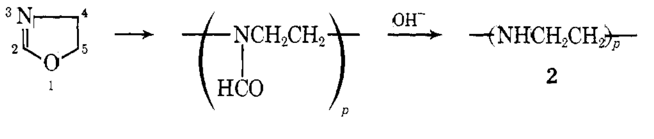
Communications to the Editor

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]



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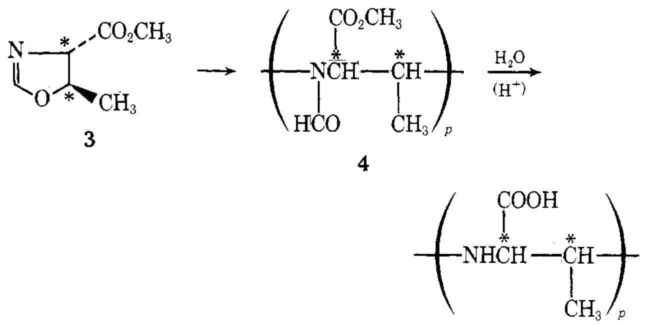
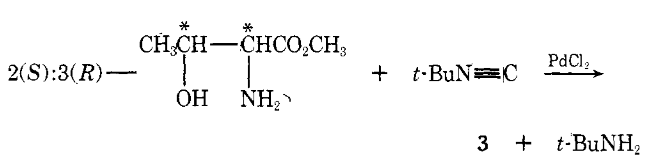


3 **4** **5**



$$2(S){:}3(R)\text{—}\underset{\text{OH}}{\overset{*}{\mathrm{CH_3CH}}}\text{—}\underset{\text{NH}_2}{\overset{*}{\mathrm{CHCO_2CH_3}}} + t\text{-BuN}{\equiv}\text{C} \xrightarrow{\text{PdCl}_2} \mathbf{3} + t\text{-BuNH}_2$$

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).

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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)