Synthesis of Poly(4-vinyl-1,4-butyrolactone-*co*-cyanoethylene)

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ABSTRACT: Copolymerization of 4-vinyl-1,4-butyrolactone (**1**) and cyanoethylene (**2**) initiated
by 2,2′-azobisisobutyronitrile were carried out. The following reactivity ratios were found for the
bulk copolymerization at 50°C for **1**, $r_1 = 0.004$, and for **2**, $r_2 = 4.4$. Radical reactivity indices and
frontier electron densities for **1**, **2**, and 3-vinyl-1,4-butyrolactone were calculated.
    KEY WORDS   Poly(4-vinyl-1,4-butyrolactone-*co*-cyanoethylene) / Copoly-
merization / Radical Reactivity Ratio / Radical Reactivity Index / Frontier
Electron Density /

The interest in the lactone function in the polymer
chain originates from its ring-opening and ring-
closing reactions. Some lactone-containing vinyl
polymers such as poly(diketene-*co*-cyanoethylene),[1]
poly(diketene-*co*-chloroethylene),[2]   poly(diketene-
co-styrene),[3]   poly(4-vinyl-1,4-butyrolactone-*co*-
4(5)-vinylimidazole),[4] and poly(3-vinyl-1,4-butyro-
lactone-*co*-cyanoethylene),[5] have already been in-
vestigated. The latter two copolymers have the
lactone moieties in side chains. The last polymer was
investigated with emphasis on its active- and
selective-transport of metal ions.[6] In the present
paper, the radical copolymerization of 4-vinyl-1,4-
butyrolactone (**1**) and cyanoethylene (**2**) initiated by
2,2′-azobisisobutyronitrile is described. In addition,
radical reactivity indices and frontier electron
densities for 4-vinyl-1,4-butyrolactone (**1**), cyano-
ethylene (**2**), and 3-vinyl-1,4-butyrolactone are
presented.

EXPERIMENTAL

Materials

4-Vinyl-1,4-butyrolactone (**1**) was synthesized
from butadiene oxide and diethyl malonate[7]; bp
62—69°C [3 mmHg (0.4 kPa)]. Cyanoethylene (**2**)
was purified in the usual manner.

Polymerization

Various amounts of **1** and **2** with various molar
ratios were placed in an ampule with 0.5 wt% of 2,2′-

azobisisobutyronitrile and sealed under nitrogen
atmosphere. The polymerization was carried out at
50°C under stirring. When the viscosity of the
reaction mixture had slightly increased, the mixture
was poured into diethyl ether and filtered. The
residual precipitate was collected. No residual ma-
terial was found in the filtrate.

Polymer Composition

The chemical composition of the copolymer was
determined by elemental analyses of carbon and
nitrogen.

Viscosity Measurement

The viscosity was measured with a $0.0004\,\mathrm{g\,cm^{-3}}$
solution of *N,N*-dimethylformamide at 25°C.

Spectroscopic Measurement

Infrared spectra were recorded on a Hitachi EPI-
G2 spectrophotometer.

Calculation

All the calculations have been carried out by the
use of the INDO MO method.[8] The radical reactivity
index (RRI), which is the measure of the reactivity of
the monomer toward the radical, is defined by

$$\mathrm{RRI} = \sum_i^{\mathrm{occ}} \frac{(C_r^{(i)})^2}{\lambda - \varepsilon_i} + \sum_j^{\mathrm{uno}} \frac{(C_r^{(j)})^2}{\varepsilon_j - \lambda} \qquad (1)$$

where $C_r^{(i)}$, $C_r^{(j)}$ are the coefficients of the rth $2p\Pi$

atomic orbital in the ith and jth MOs, respectively, whose energies are ε_i and ε_j, respectively, and λ denotes the energy of the singly-occupied MO of the attacking radical.

The frontier electron density $(f_r^{(R)})$ is defined by

$$f_r^{(R)} = (C_r^{(HO)})^2 + (C_r^{(LU)})^2 \qquad (2)$$

where $C_r^{(HO)}$ and $C_r^{(LU)}$ are the coefficients of the rth $2p\Pi$ atomic orbital in the highest-occupied and lowest-unoccupied MOs, respectively.

RESULTS AND DISCUSSION

The results of the copolymerization are shown in Table I. Molecular weights of the copolymers were

Table I. Result of the copolymerization of 4–vinyl–1,4–butyrolactone(**1**) and cyanoethylene(**2**)[a]

Expt No.	Monomer		AIBN/mg	Time/h	Yield/g	Elementary analysis/%		Mol fraction of **1** in		η_{sp}/c
	1/g	2/g				C	N	Monomer	Polymer	
1	0.255	1.055	7.6	1.4	0.023	67.03	24.45	0.103	0.032	1.90
2	0.382	0.916	6.9	2.5	0.016	66.56	23.31	0.165	0.052	1.00
3	0.619	0.687	6.9	4.0	0.015	66.29	21.88	0.299	0.082	0.55
4	0.766	0.544	6.6	17.9	0.058	66.86	19.77	0.400	0.136	0.40
5	0.878	0.422	6.6	44.1	0.062	66.56	17.34	0.496	0.190	0.55
6	0.982	0.309	6.8	44.2	0.051	65.33	16.52	0.600	0.212	0.40
7	1.072	0.211	6.8	44.1	0.022	65.09	15.40	0.697	0.243	0.08
8	1.183	0.111	6.9	44.5	0.019	64.16	12.02	0.835	0.350	0.10
9	1.242	0.067	6.7	44.7	0.013	64.01	10.31	0.898	0.414	0.13

[a] Polymerization temp, 50°C. Reduced viscosity was measured at $c = 0.0004\,\mathrm{g\,cm^{-3}}$-DMF, 25°C.
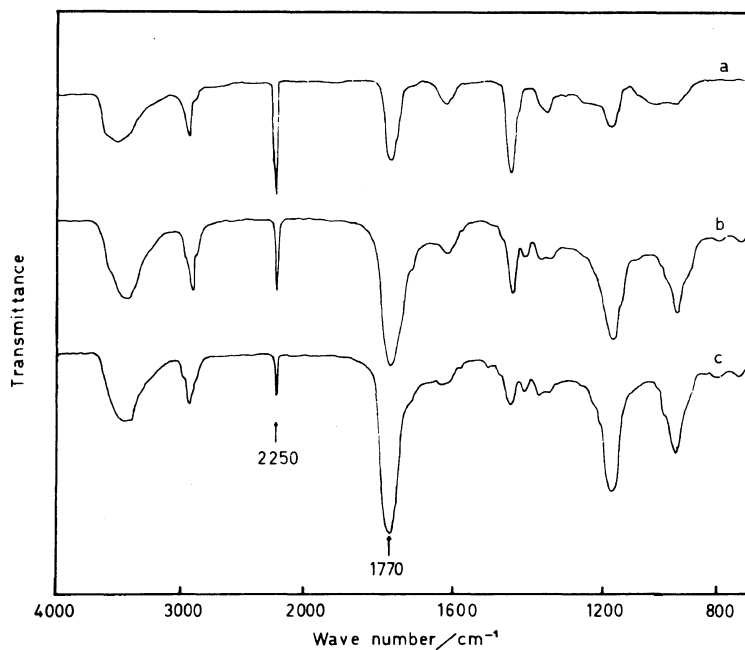
Figure 1. IR spectra of poly(**1**-*co*-**2**)s in KBr: a, **1**:**2**=3.2:96.8; b, **1**:**2**=24.3:75.7; c, **1**:**2**=41.4:58.6; thickness, 0.24 mm (1 mg polymer/200 mg KBr).

not always high. The reduced viscosity decreased with increasing the content of **1** in the poly(**1**-*co*-**2**). The number-average molecular weight, $\bar{M}_n$, of the sample (Exptl. No. 7, which has the lowest reduced viscosity) was estimated to be *ca.* 1200 for $\bar{M}_n$, adopting the molecular weight–viscosity relationship for polycyanoethylene.[9] The homopolymerization of **1** had effectively stopped after 5 days.

Figure 1 shows the IR spectra of copolymers. The characteristic absorptions at $2250\,\mathrm{cm}^{-1}$ ($-\mathrm{C}\equiv\mathrm{N}$) and $1770\,\mathrm{cm}^{-1}$ (lactone) are shown in Figure 1. These two characteristic absorptions were identical with those of poly(3-vinyl-1,4-butyrolactone-*co*-cyanoethylene).[5]

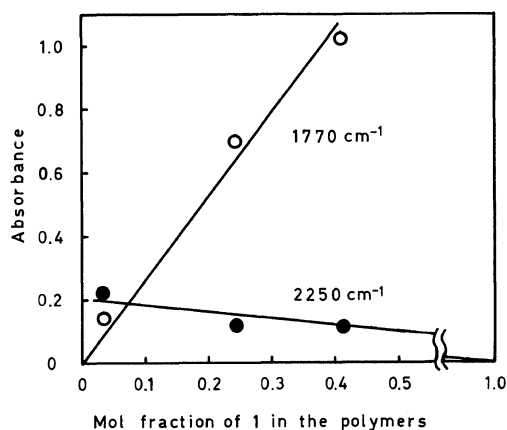In Figure 2, these absorptions are shown quantitatively.

Figure 2. Absorbances at $1770\,\mathrm{cm}^{-1}$ and $2250\,\mathrm{cm}^{-1}$ of poly(**1**-*co*-**2**)s against their composition.
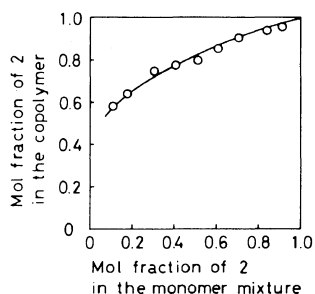

Figure 3. Polymer *vs.* monomer composition in the copolymerization of 4-vinyl-1,4-butyrolactone (**1**) and cyanoethylene (**2**); polymerization temp, 50°C; initiator, 2,2′-azobisisobutyronitrile.

Figure 3 shows the copolymer composition dia-

Table II. Radical reactivity indices (RRI) and frontier electron densities $(fr^{(R)})$ for **1**, **2**, and **3**

Position	RRI[a]	$fr^{(R)}$
a	2.51	0.442
b	2.77	0.597
c	2.50	0.525
d	2.82	0.786
e	2.59	0.360
f	2.78	0.458

[a] RRI was calculated, taking the value $\lambda = -0.15$ a.u.
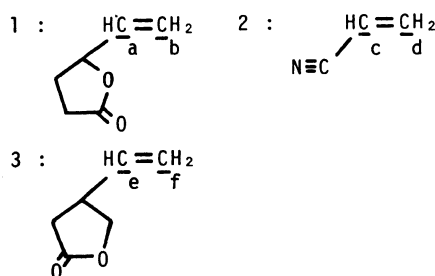
gram. The radical reactivity ratios were determined to be $r_1 = 0.004$ and $r_2 = 4.4$ by the Kelen–Tüdõs method.[10] The radical reactivity ratio of **1** was lower than that of 3-vinyl-1,4-butyrolactone (**3**) in the copolymerization with **2**. In general, the degree of polymerization of poly(**1**-*co*-**2**) was lower than that of poly(**3**-*co*-**2**).[5]

In Table II, radical reactivity indices (RRI) and frontier electron densities $(f_r^{(R)})$ are shown; here the oribital energy of the radical, λ, which attacks the monomer, is assumed to be -0.15 a.u. Even if the orbital energy of the attacking radical was assumed to be -0.05, -0.10, -0.20, or -0.25 a.u., these trends were similar to that in Table II. RRI indicates that the reacting position of the monomer toward the growing chain radical is mostly often at the *d*-carbon in **2** and at the *b*-carbon in **1**. Accordingly, the polymer structure is to be a head-to-tail one and the growing chain terminals are to be
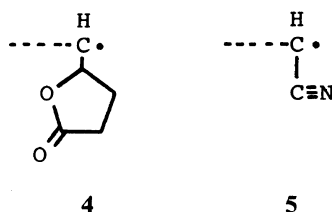
The growing chain terminal structure, 4, is readily converted into allylic radical by losing its 4-hydrogen; the growing chains, 4 and 5, may also subtract the 4-hydrogen of another molecule of 1. Accordingly, the molecular weight of the copolymer decreased with the feed of 1.

When this copolymer was immersed in $1 \, mol \, dm^{-3}$ alkaline solution, it dissolved. Acidification of the solution then caused precipitates to form. Thus, the ring-opening and the ring-closing reactions of the lactone moiety in the polymer take place with alkali and acid in analogy with the processes involving poly(3-co-2).[5].

APPENDIX

From the MO perturbation theory,[11] the stabilization of the composite reacting system to the delocalization of electrons between the radical, R, and the closed-shell monomer, M, is given by

$$D \simeq 2 \left\{ \sum_i^{occ} \sum_j^{uno} \frac{(\sum_r C_r^{(i)} C_{r'}^{(l)} \gamma_{rr'}^{(i)})^2}{I_{Mi}^{(R)} - E_{Rl}^{(M-i)}} \right. $$
$$ + \sum_k^{occ} \sum_j^{uno} \frac{(\sum_r C_r^{(j)} C_{r'}^{(k)} \gamma_{rr'}^{(k)})^2}{I_{Rk}^{(M)} - E_{Mj}^{(R-k)}} \right\} $$
$$ + \left\{ \sum_i^{occ} \frac{(\sum_r C_r^{(i)} C_{r'}^{(o)} \gamma_{rr'}^{(i)})^2}{I_{Mi}^{(R)} - E_{Ro}^{(M-i)}} + \sum_j^{uno} \frac{(\sum_r C_r^{(j)} C_{r'}^{(o)} \gamma_{rr'}^{(o)})^2}{I_{Ro}^{(M)} - E_{Mj}^{(R-o)}} \right\} \quad (3) $$

where $C_r^{(i)}$ and $C_r^{(j)}$ are the coefficients of the AO χ_r in the occupied MO ϕ_i and the unoccupied MO ϕ_j of the monomer, respectively; $C_{r'}^{(k)}$, $C_{r'}^{(l)}$, and $C_{r'}^{(o)}$ are the coefficients of the AO $\chi_{r'}$ in the occupied MO $\psi_{k'}$, the unoccupied MO ψ_l, and the singly-occupied MO ψ_0 of the the radical R, respectively; $\phi_i = \sum_r C_r^{(i)} \chi_r$, $\psi_l = C_{r'}^{(l)} \chi_{r'}$ etc.

The integral, $\gamma_{rr'}$, represents the interaction between the reaction centers r and r' through the overlap between the AOs χ_r and $\chi_{r'}$; $\gamma_{rr'} = \int \chi_r h \chi_{r'} d\tau$.

$I_{Mi}^{(R)}$ is the ionization potential of the MO ϕ_i of the monomer M in the neutral field of the attacking radical R, and $E_{Rl}^{(M-i)}$ is the electron affinity of the

MO ψ_l of the radical R under the influence of the cationic species $(M-i)$ generated by the removal of an electron from the MO ϕ_i of M. The summation $\sum^{occ}$ and $\sum^{uno}$ cover all the occupied and unoccupied MOs, respectively.

If we assume that the singly occupied MO of the radical, ψ_o, is localized at the radical center, as is often the case, the first and second terms in eq 3 vanish. Because the interaction integral, $\gamma_{rr'}$, between the reaction centers of the radical and the monomer is approximately common to all the MO combinations, the radical reactivity index (RRI), which is the measure of the reactivity of the monomer toward the radical, is defined by eq 1. Using the self-consistent field MO energies, the denominator of eq 3 is represented by

$$ I_{Mi}^{(R)} - E_{Rl}^{(M-i)} \simeq \varepsilon_{Mi} - \varepsilon_{Rl} + (ii \mid ll) $$

where $(ii \mid ll)$ is the coulombic repulsion integral between the electrons in the MO ϕ_i and the MO ψ_l. The coulombic repulsion for the ordinary reaction system is about 0.1 a.u. In the present paper, the repulsion term was disregarded because the attacking radical has not been identified.

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