the phenolates appeared in the long wavelength region and varied from 532–586 nm for the same type of electronic transition. Similar observations have been reported for mono-[1f] and dibasic[1e] chromoacerands-amine systems. Significant differences (up to 11 nm) in λ_{max}'s between diastereomeric sets of the salts have been observed for several acerand-amine combinations (Figure 1). *When the guests were (S)-(−)-α-phenethylamine ((S)-**4**), (S)-(−)-1-(1-naphthyl)ethylamine ((S)-**5**), D-valinol ((R)-**8**), and (1R,2R)-(−)-norpseudoephedrine (**11**), indicator (SSSS)-**2** caused blue-shifts of the absorption bands compared with the enantiomer (RRRR)-**2**. A similar blue-shift was also observed with the (SS)-**1**:(R)-**5** combination.* As expected, utilization of (*RR*)-**1** and (*RRRR*)-**2** brought about the reverse results so that several "crossings" are noted in Figure 1.[6] These blue-shifts are the first observation of enantiomeric amine-selective coloration.

The second step of this work is to predict the structures of the colored saltexes in ethanol. From examination of CPK molecular models it is predicted, as described below, that the most stable geometries of the saltexes consisting of **2**–**4**, –**5**, –**8**, and –**11** combinations are **13**–**16** as shown in Figure 2. In other words, *(SSSS)-**2** shows better complementarity than the (RRRR)-isomer to (S)-**4**, (S)-**5**, (R)-**8**, and **11**, and (SS)-**1** fits (R)-**5** better than the (RR)-isomer does.* Here, the assumption is made that the phenolate oxygen atom participates in hydrogen bonding between the host and guest. This assumption seems to be quite reasonable in view of the high hydrogen bond-acceptor ability of the negatively charged oxygen and has been verified in the crystal structures of saltexes.[1e,f,7] Applying the well-known three-point binding model[3b] to the (*SSSS*)-**2**:**4** system gives the predicted geometry **13**[8] where the smallest substituent, hydrogen, occupies the most hindered area. Judging from the steric requirements of this model, the Ph group at C_3 in **13** must be more effective than the Ph group at C_{12} as a chiral barrier against the guest. However, the same binding model would be unfavorable for the **2**:**5** system because of the more bulky 1-naphthyl group, which should prefer to occupy the least hindered area in structure **14** as predicted from the two-point binding mode.[10] Applying the same binding model to **1**:**5** systems predicts better complementarity of (*R*)-**5** to (*SS*)-**1** rather than the (*RR*)-isomer. A slim ethanolamine skeleton would exactly fit a three-point binding model as shown in **15**[8] and **16**,[8] where an additional hydrogen bonding between the phenolate oxygen and the alcoholic OH group should stabilize these saltexes further. Another conformer produced by rotation about the C–C bond axis of the guest in **15** should be less stable due to steric hindrance between the phenyl group at C_3 and the R^2 group. Therefore, it is easily understandable from the predicted structures **15** and **16** that (*R*)-**8** and **11** which bear substituents R^1 and R^2 in less hindered positions should show better complementarity to (*SSSS*)-**2** than the (*RRRR*)-isomer.

The final step is to correlate the observed blue-shift with the difference in the structure or the host–guest complementarity between the two diastereomers. It is noted that *the indicator-species combinations for which better host–guest complementarity is predicted are those combinations which exhibit the blue-shift.* This is consistent with the following explanation for the blue-shift. Hydrogen bonding between the phenolate oxygen of the host and an N^+H hydrogen of the guest in **13**–**16** stabilizes the energy of the polar ground state more than that of the less polar excited state of the chromophore. Similar blue-shifts induced by metal[11] and ammonium ions have been reported in other dye systems.[1] Further, a parallel relationship between the blue-shift and thermodynamic stability in chloroform, which increases with the better host–guest complementarity, has been found.[1e,f]

Thus we have demonstrated that enantiomeric amine-selective coloration can be obtained. By synthesizing the indicator as an enantiomeric pair, we have overcome the troublesome problem that both enantiomers of the species to be analyzed are not always available. Utilization of the present acerands as color indicators to judge the absolute configuration of chiral amines depends on the reliability of the structures predicted for their ammonium saltexes.

---

(6) Such crossings provide strong evidence for the reliability of the experiments.

(7) (a) Goldberg, I. *Acta Crystallogr.* **1975**, *B31*, 2592–2600. (b) Browne, C. M.; Ferguson, G.; McKervey, M. A.; Mulholand, D. L.; O'Conner, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703–2712.

(8) This structure is the same as that predicted by chiral twist theory,[9] a general rationalization for enantioselective complexation involving chiral 18-crown-6 analogues.

(9) Sutherland, I. O., private communication.

(10) The other two possible candidates involving O_5 or O_8 would be unfavorable because of the steric interactions between the Ph group at C_3 and the guest or absence for additional binding with the benzylic oxygens.

(11) (a) Dix, J. P.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 857–859. (b) For a review: Löhr, H.-G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65–72.

Selective Alternating Copolymerization of Allene Derivatives through Macro Allyl Zwitterion

Jiro Mizuya, Tsutomu Yokozawa, and Takeshi Endo*

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227, Japan

Received August 2, 1988

Recent investigations in our laboratory have focused on the features of the polymerization of substituted allenes, which are regarded as vinyl monomers bonded to another methylene carbon. We have recently reported that allene derivatives undergo radical polymerization to obtain polymers bearing *exo*-methylene groups attached to the polymer backbone.[1] In the course of research on the copolymerization of monosubstituted allenes, we found that an allene bearing an electron-donating group reacted with one bearing an electron-withdrawing group to give copolymer under mild conditions. Herein we report the spontaneous copolymerization of methoxyallene **1**[2] with cyanoallene **2**,[3] which yields 1:1 copolymer irrespective of the feed ratio of both allenes.

The reaction of **1** with **2** was carried out at 60 °C in bulk to afford the copolymer of **1** and **2**.[4] Some peculiar features of this copolymerization are as follows. (1) When an equimolar mixture of **1** and **2** was allowed to react, the rate of consumption of **1** and that of **2** was equal, and the copolymer consisted of **1** and **2** with the ratio 1:1 irrespective of the reaction time. (2) The number-average molecular weight ($\bar{M}_n$) of polymer obtained increased with conversion, especially the increase of $\bar{M}_n$ was accelerated in high conversion. (3) When **1** was allowed to react with 3 equiv of **2**, the rate of consumption of **1** and that of **2** was also equal, and the lack of **1** stopped completely the reaction even though 66% of **2** remained in the reaction mixture (Figure 1). In the reaction of 3 equiv of **1** with **2**, similar behavior was observed. (4) When the reaction was carried out in various feed ratios of **1** to **2**, the composition of the copolymers constantly remained as the ratio 1:1 irrespective of the feed ratio, while yields became maximum in the feed ratio 1:1 (Figure 2). Since the corre-

---

(1) Yokozawa, T.; Tanaka, M.; Endo, T. *Chem. Lett.* **1987**, 1831. Mizuya, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Lett. Ed.*, in press.

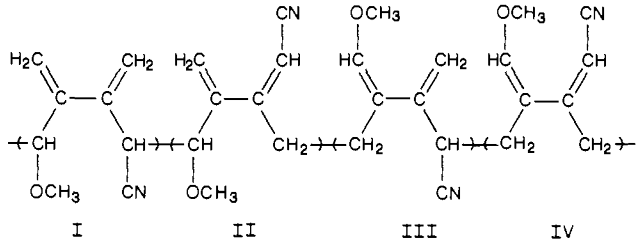
(2) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Ed.* **1978**, *16*, 615.

(3) Kuritz, P.; Gold, H.; Disselnkotler, H. *Ann. Chem.* **1959**, 624.

(4) Four sealed polymerization tubes containing **1** (0.30 g, 4.3 mmol) and **2** (0.28 g, 4.3 mmol) were heated at 60 °C for 0.5, 1, 2, and 3 h, respectively. The polymers were purified by dissolution in dichloromethane, followed by precipitation with diethyl ether (the soluble polymers were converted into gel polymer during isolation). The precipitated materials and the ether layer were dried under reduced pressure [the yield and polymer composition (estimated from elemental analysis) show after isolation of the polymer, spectral data (^1H NMR and IR) of soluble polymer were measured, and Mn was estimated by GPC (based on Poly-St) before precipitation]: (0.5 h) conversion = 59%, yield = 3%, $\bar{M}_n = 2.0 \times 10^4$, 1:2 = 53:47; (1 h) 73%, 7%, 3.7×10^4, 51:49; (2 h) 81%, 13%, 4.7×10^4, 52:48; (3 h) 86%, 15%, 5.0×10^4, 51:49.

0002-7863/89/1511-0743$01.50/0

Scheme I



sponding vinyl analogues (vinyl ethers and acrylonitrile) cannot polymerize under the same conditions, these characteristic features of the copolymerization of **1** and **2** are considered to result from the substituted allene systems.

The ^{1}H NMR spectrum of copolymer obtained shows the signal corresponding to the diene protons at 6.6–6.0 ($>\mathrm{C{=}C}H\mathrm{{-}OMe}$ and/or $>\mathrm{C{=}C}H\mathrm{{-}CN}$) and 5.8–4.8 ppm ($>\mathrm{C{=}C}H_2$) and the signal assignable to the vinyl methoxy protons ($>\mathrm{C{=}C{-}O{-}C}H_3$) and allyl methoxy protons ($>\mathrm{C{=}C{-}C{-}O{-}C}H_3$) at 3.8–3.6 and 3.6–3.1 ppm, respectively. The IR spectrum shows the characteristic absorptions at 1675 and 1620 cm^{-1} due to the diene structure and vinyl ether and allyl ether at 1240, 1140, and 1100 cm^{-1}, respectively.[5] From these spectral data, the copolymer consisted of four types of diene units (I, II, III, IV), and the ratio of I–IV was 7:21:10:62[6] (Scheme I).

From the characteristic features of this copolymerization and the structure of the copolymer, we propose that zwitterion **4** generated from **1** and **2** is the key intermediate. Consequently, the reaction of **1** with **2** was carried out in methanol to obtain diene **3** formed by trapping of **4** with methanol in high yield.[7] The proposed polymerization process shown in Scheme II involves generation of stable allyl zwitterion **4** through the attack of the center carbon of nucleophilic allene **1** on the center carbon of electrophilic allene **2**, followed by successive propagation steps involving selective combination of **4** with each other and coupling of macro zwitterion without accompanying homopolymerization of **1** and/or **2** (Scheme II). To our knowledge, the polymerization behavior described above represents the first example of spontaneous polymerization of allene derivatives involving allyl zwitterions.

Although such macro zwitterionic copolymerization has been studied by using heterocyclic monomers and/or vinyl monomers (*N*-vinylcarbazole, tetracyanoethylene, etc.), it is difficult to obtain alternating copolymers with high molecular weight without accompanying homopolymerization of the more polymerizable monomer.[8] On the other hand, in this copolymerization, alternating copolymer with higher molecular weight ($\bar{M}_n = 5.0 \times 10^4$) can be selectively obtained irrespective of the allene monomer feed ratio, through stabilized allyl zwitterion[9] (allyl carbanion and allyl carbenium ion). Further investigation on the copolymerization of **1** with electrophilic compounds is now in progress and will be reported soon.

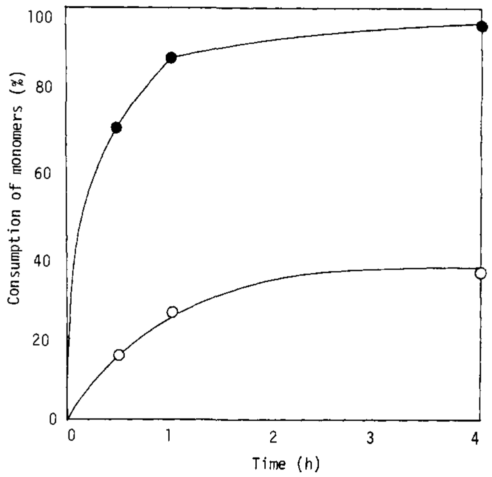


Figure 1. Time versus consumption of monomers on the copolymerization of **1** with 3 equiv of **2** in bulk at 60 °C: **1** (●); **2** (○).

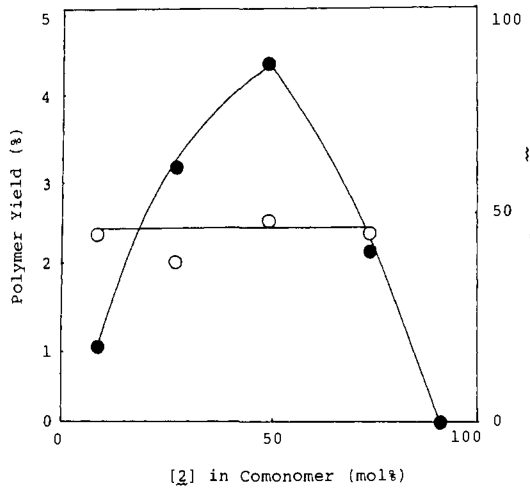
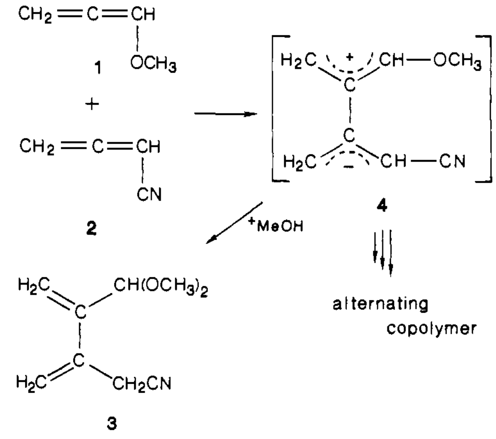


Figure 2. Effects of monomer feed ratio on the polymer yield (●) and on the polymer composition (○) (in bulk at 60 °C for 1 h).

Scheme II



Registry No. (**1**) (**2**) (copolymer), 118018-53-4; **3**, 118018-54-5; **2**, 1001-56-5; **1**, 13169-00-1.

---

[5] Moazzam, G.; Jacobs, T. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *108*, 361.

[6] Copolymerization of **1** (0.34 g, 4.9 mmol) and **2** (0.32 g, 4.9 mmol) was carried out at 60 °C for 1 h in a sealed tube. The polymer was purified by dissolution in dichloromethane, followed by precipitation with CD_3OD. The methanol layer was concentrated under reduced pressure to give soluble polymer (0.42 g; yield = 62%). The contents of the units in the polymer were estimated by ^{1}H NMR analysis (based on the following chemical shift value): 6.6–6.0 ($\mathrm{C{=}C}H\mathrm{{-}OMe}$ and/or $\mathrm{C{=}C}H\mathrm{{-}CN}$), 5.8–4.8 ($\mathrm{C{=}C}H_2$), 4.8–3.8 ($\mathrm{C{=}C{-}C}H\mathrm{{-}OMe}$), 3.8–3.6 ($\mathrm{C{=}C{-}OC}H_3$) 3.6–3.1 ($\mathrm{C{=}C{-}C{-}OC}H_3$), 3.3–3.0 ($\mathrm{C{=}C{-}C}H\mathrm{{-}CN}$), 3.0–2.0 ($\mathrm{-C}H_2\mathrm{-}$) ppm.

[7] Reaction of **1** (0.64 g, 9.1 mmol) and **2** (0.59 g, 9.1 mmol) was carried out in dry methanol (6 mL) at 40 °C for 24 h. The methanol solution was concentrated under reduced pressure to give **3** (74%). MS (*m/s*) 167 (M^+); IR (neat) 2830, 1450, 2245, 1655, 1600, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) 5.52–5.05 (m, 4 H), 4.85 (s, 1 H), 3.32, 3.28 (2 s, 8 H), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 141.6, 134.3, 117.8, 103.2, 117.0, 110.0, 53.4, 23.4 ppm.

[8] Saalfrank, R. W. *Tetrahedron Lett.* **1973**, *40*, 3985. Moriconi, E. J.; Kelly, J. F. *J. Org. Chem.* **1968**, *33*, 3036.

[9] Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1972**, 354. Goto, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.