Single-feed one-step block copolymerization of *n*-octyloxyallene with phenylallene using π-allylnickel as initiator

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The π-allylnickel initiated block copolymerization of *n*-octyloxyallene and phenylallene takes place in one step from a single-feed mixture of the two monomers.

The living polymerization technique is the most prominent method to obtain well-defined block copolymers.[1] Generally, two monomers are fed stepwise as the polymerization progresses, except in a few examples. Saegusa *et al.* reported the 'one-shot block copolymerization' of 2-alkyl-2-oxazoline with 2-perfluoroalkyl-2-oxazoline,[2] which involves the change of the propagating species from the ionic to the covalent form. Feast *et al.* also reported the successful one-shot block copolymerization of *syn*- and *anti*-7-methylnorbornene using a Schrock molybdenum alkylidene initiator,[3] where the large difference in polymerizability of the two monomers assisted the block copolymerization.

Herein, we describe the π-allylnickel complex initiated block copolymerization of *n*-octyloxyallene **2** with phenylallene **3** in one step from a single-feed mixture of the two monomers[4,5] (Scheme 1).

A mixture of **2** and **3** (50 equiv. each) was added to a toluene solution of $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$ **1** and the polymerization was performed for 12 h. As a result, a copolymer (M_n = 20 100, M_w/M_n = 1.15) was obtained in 94% yield, whose composition was poly(**2**):poly(**3**) = 49 : 51 (determined by ^{1}H NMR spectroscopy) in good accordance with the monomer feed ratio. The monomer conversion, determined by GC, gave interesting information on the copolymerization process (Fig. 1).†

The specific consumption of **2** took place at the initial stage of the polymerization, meanwhile **3** was not converted at all. However, when **2** had been consumed completely, the slow polymerization of **3** started to give a copolymer with a high block sequence. By quenching the copolymerization of **2** with **3** (50 equiv. each) in the initial stages (*i.e.* at 0 °C for 10 min) by pouring the reaction mixture into large amount of MeOH–H_2O (1 : 1), a polymer (M_n = 9450, M_w/M_n = 1.15) was obtained in 54% yield, which was composed solely of a poly (**2**) segment (determined by ^{1}H NMR spectroscopy).[6] This experiment also supports the efficient formation of a block copolymer.

The unexpected formation of the block copolymer cannot be explained fully by the difference in polymerization rate of the two monomers [k_{obs} (**2**) = 9.94×10^3 and k_{obs} (**3**) = 0.14×10^3 l mol^{-1} h^{-1}; k_{obs} (**2**)/k_{obs} (**3** = *ca.* 70]. The observed kinetic coefficient of **2** is not influenced by **3**, because k_{obs} (**2**) in the early stage of the copolymerization (9.94×10^3 l mol^{-1} h^{-1}) is comparable to that in the homopolymerization of **2**. The result clearly indicates that the concentration of the active species (most probably the nickel complex coordinated with **2**) is not affected by **3**. Namely, it can be taken to mean that the coordination equilibrium of the nickel complex with the monomers is shifted considerably to coordinated with **2** in the copolymerization, which promotes the specific polymerization of **2** in the initial stages. Further work on the copolymerization of various monomer combinations and a mechanistic investigation are in progress.

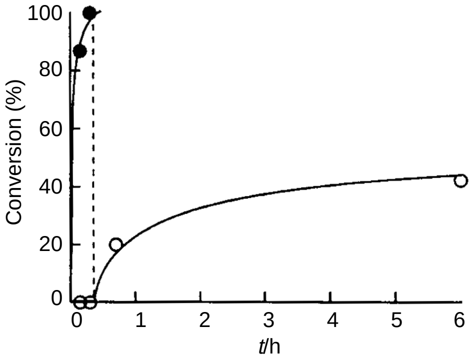

Fig. 1 Time *vs.* conversion curves for (●) **2** and (○) **3** in the copolymerization by **1** at 0 °C ($[\mathbf{2}]_0 = [\mathbf{3}]_0 = 5.0 \times 10^{-2}$ M, [Ni] = 1.0×10^{-3} M)

Notes and References

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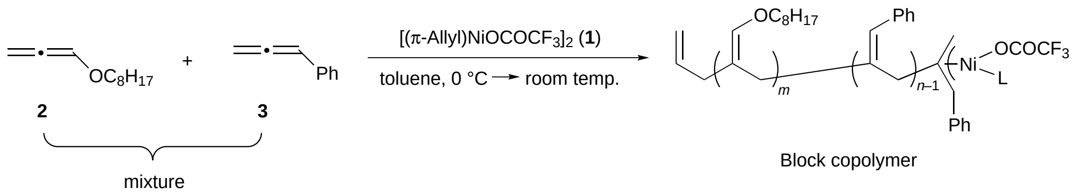
‡ Estimation of the kinetic coefficients (typical procedure): The copolymerization of **2** with **3** ($[\mathbf{2}]_0$/[Ni] = $[\mathbf{3}]_0$/[Ni] = 50, [Ni] = 1.0×10^{-3} M) by **1** was performed at 0 °C in toluene containing *n*- tetradecane (2.0×10^{-3} M) as an internal standard. After designated reaction periods, a small portion of the reaction mixture was sampled with the syringe (*ca.* 10 μl) and the monomer conversions were estimated by GC analysis.

1 See, for example: A. S. Hoffmann and R. Bacckai, in *Highpolymers, Vol. XVIII, Copolymerization*, ed. G. E. Ham, Wiley, New York, 1964, ch. 6, p. 135; I. Goodman, in *Development in Block Copolymer I*, ed. I. Goodman, Elsevier, Essex, 1982, ch. 5, p. 127; D. B. Johns, R. W. Lenz, and A. Luick, in *Ring-Opening Polymerization, Vol. I*, ed. K. J. Ivin and T. Saegusa, Elsevier, London, 1984, ch. 5, p. 218; R. N. Young, *Trends Polym. Sci.*, 1993, **1**, 149.



Scheme 1

2 T. Saegusa, Y. Chujo, K. Aoi, and M. Miyamoto, *Makromol. Chem., Macromol. Symp*., 1990, **32**, 1.

3 W. J. Feast, V. C. Gibson, K. J. Ivin, E. Khosravi, A. M. Kenwright, E. L. Marshall and J. P. Mitchell, *Makromol. Chem*., 1992, **193**, 2103.

4 For the living polymerization of allene derivatives, see: I. Tomita, Y. Kondo, K. Takagi and T. Endo, *Macromolecules*, 1994, **27**, 4413; K. Takagi, I. Tomita and T. Endo, *Maclomolecules*, 1997, **30**, 7386.

5 We have recently reported the two-feed block polymerization of alkoxyallenes with phenylallene by a π-allylnickel catalyst, in which block copolymers with controlled segment lengths could be successfully obtained by using additives (PPh_3 or CuI) over the course of the polymerization. See: K. Takagi, I. Tomita and T. Endo, *Polym. Bull*., in the press.

6 The yield of 54% corresponds to 91 wt% of **2**. Namely, **3** was untouched at least until the conversion of **2** reached to 91%.

Received in Cambridge, UK, 8th December 1997; 7/08786A