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Polymerization of Cyclooctyne with Late Transition Metal Catalysts

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Acetylenic compounds provide high molecular weight polymers in good yields in the presence of groups 5 and 6 transition metal catalysts based on W, Mo, Ta, and Mo.[1] On the contrary, despite the excellent ability of late transition metal catalysts such as Pd and Ni to induce polymerizations of various cyclic and acyclic monomers, they do not suit acetylene polymerization. This is because oligomerization dominates over polymerization to give cyclo- and linear oligomers as main products.[2] Exceptional examples are given only by Rh catalysts that polymerize monosubstituted acetylenes via the insertion mechanism, giving cis−transoidal polymers.[3] However, even Rh catalysts are unfortunately inactive for the polymerization of disubstituted acetylenes. Thus, it is a challenging and interesting subject to polymerize acetylenic disubstituted monomers with late transition metal catalysts, especially with Pd and Ni catalysts, because copolymerization of acetylenes with a wide range of monomers would be possible. In addition, highly advanced synthetic chemistry using Pd and Ni catalysts will also make it possible to achieve the end functionalization of substituted polyacetylenes. To accomplish this purpose, we selected cyclooctyne (CyOc) as a monomer because it shows high polymerizability owing to its very large ring strain (∼9 kcal/mol)[4] and because, if polymerization proceeds by the insertion mechanism, the tetrasubstituted olefinic structure of the polymer main-chain would retard cyclooligomerization.

Indeed, we found that CyOc, which is one of many disubstituted acetylenes, gave polymer in good yield by using late transition metal catalysts including Pd, Ni, and Rh catalysts (Table 1).[5] Polymerization proceeded extremely fast in the absence of basic ligands such as PPh_3 and dba (runs 1, 4, 5, 8, and 9); instantaneous gelation took place just after feeding CyOc to catalyst solutions. Pd catalysts tended to afford polymers in good yields as compared with Ni catalysts. Interestingly, $[(nbd)RhCl]_2-Et_3N$, which does not catalyze the polymerization of disubstituted acetylenes, did polymerize CyOc very rapidly to give polymer in good yields. This is the first example of the Rh-catalyzed polymerization of disubstituted acetylenes. $[(nbd)RhCl]_2$-catalyzed polymerization of monosubstituted acetylenes generally requires polar additives such as Et_3N to enhance the rate of polymerization.[3] This is because Et_3N promotes the dissociation of the dimeric Rh complex to provide a cationic complex which works as active species. Emphasis should be placed on the fact that, in the homopolymerization of CyOc with $[(nbd)RhCl]_2$, we observed no evident efficacy of Et_3N; exothermic polymerization of CyOc readily occurred with $[(nbd)RhCl]_2$ even in the absence of Et_3N.

Table 1. Homopolymerization of CyOc with Various Late Transition Metal Catalysts[a]

run	catalyst	yield (%)[b]
1	$PdCl_2(PhCN)_2$	80
2	$PdCl_2(PPh_3)_2$	80
3	$Pd_2(dba)_3$	78
4	$Pd(OTs)_2(CH_3CN)_2$	67
5	$Ni(cod)_2$	50
6	$NiCl_2(PPh_3)_2$	39
7	$Ni(acac)_2$	0
8	$[(nbd)RhCl]_2$	70
9	$[(nbd)RhCl]_2$-Et_3N[c]	74

[a] In toluene, 30 °C, 24 h, [M] = 1.0 M, [M]/[Cat] = 20. [b] Methanol-insoluble part. [c] $[Et_3N]/[Cat] = 2.0$.

Table 2. Copolymerization of CyOc with PA Using $[(nbd)RhCl]_2$ [a]

run	CyOc:PA in the feed	yield (%)[b]	M_n [c]	M_w/M_n [c]	copolymer compn (CyOc:PA)[d]
1	80:20	33	insoluble		
2	70:30	38	insoluble		
3	50:50	26	19200	2.06	30:70
4	40:60	40	31700	3.61	6:94
5	30:70	43	11700	5.25	2:98

[a] In toluene, 30 °C, 24 h, $[M]_{0,total} = 0.2$ M, [M]/[Cat] = 50. [b] Methanol-insoluble part. [c] Determined by GPC (PSt standard). [d] Determined by ^1H NMR.

Since poly(CyOc) was insoluble in organic solvents such as THF, toluene, and *o*-dichlorobenzene regardless of catalyst, we investigated the copolymerization of CyOc with phenylacetylene using $[(nbd)RhCl]_2$ as catalyst to obtain soluble copolymers (Table 2). When the feed ratio of PA/CyOc was below 1, polymerization solution geled instantaneously after the addition of $[(nbd)RhCl]_2$, resulting in an insoluble polymer. On the contrary, when the ratio was higher than unity, polymerization proceeded homogeneously, leading to the formation of copolymers soluble in various organic solvents. The copolymerization behavior was further investigated by monitoring the consumption of monomers by using ^1H NMR in C_6D_6 (Figure 1). Because the polymerization of CyOc proceeded very rapidly, PPh_3 was added to retard the polymerization ($[PPh_3]/[Cat] = 2$).[6] As shown in Figure 1, CyOc completely reacted within 5 min even in the presence of PPh_3. On the other hand, PA was consumed much slower. This result suggests that blocklike copolymerization proceeded owing to a large difference in reactivity between these comonomers.

The resulting homo- and copolymers were characterized by ^1H and ^{13}C NMR and IR spectroscopies as well as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The IR spectrum of CyOc exhibited a strong absorption for the carbon−carbon triple-bond stretching at 2100 cm^{-1}, which was not observed in the spectrum of poly(CyOc).[7] This means that the carbon−carbon triple bond in the monomer certainly reacted during the polymerization. The ^1H NMR spectra of the copolymers obtained in runs 3−5, Table 2 displayed three sharp peaks attributed to the poly(PA) segment around 6−7 ppm.[7] The spectral pattern in this region was completely identical to that of

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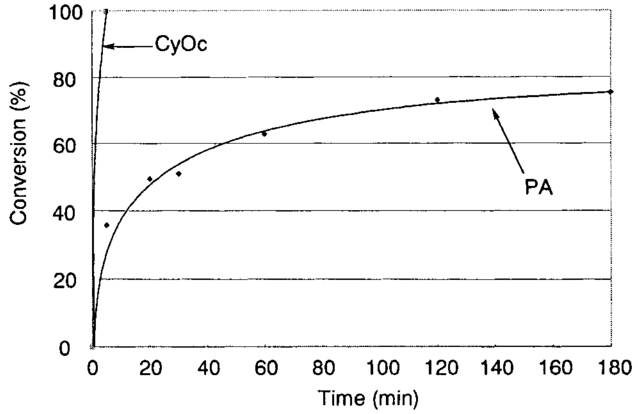

Figure 1. Time−conversion curves for the copolymerization of CyOc and PA (in C_6D_6, 30 °C, [CyOc] = [PA] = 0.25 M, $[M]_{0,\,total}$/[Cat] = 50, $[PPh_3]$/[Cat] = 2.0).

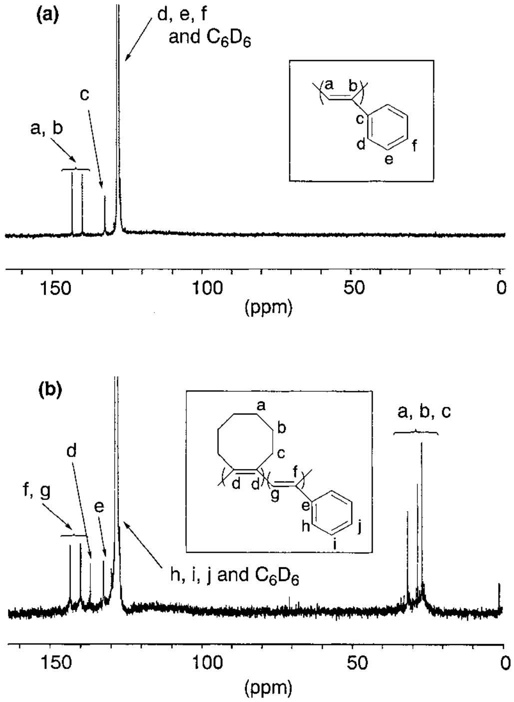

Figure 2. ^{13}C NMR spectra of (a) poly(PA) and (b) poly(CyOc-*co*-PA) (sample from run 3, Table 2) in C_6D_6.

poly(PA) prepared with Rh catalysts, which means that the poly(PA) unit selectively possesses a cis−transoidal geometrical structure. In addition to these peaks, a broad signal due to the methylene protons of the poly(CyOc) segment was observed around 1−3 ppm. Furthermore, all the GPC curves of these soluble copolymers were unimodal. It can be concluded from these results that copolymers of CyOc with PA were obtained and that the formation of the homopolymer from CyOc or PA is negligible.

The ^{13}C NMR spectrum provided us more detailed information about the structure of the copolymer (Figure 2). As illustrated in Figure 2a, cis−transoidal poly(PA) prepared with a Rh catalyst gave well-resolved signals (a−c) attributed to the olefinic and ipso carbons. These ^{13}C resonances were also observed in the spectrum of the copolymer (signals e−g in Figure 2b), meaning the selective formation of a cis−transoidal poly(PA) segment. Therefore, the other peaks observed in the spectrum of the copolymer (signals a−d) are based on the poly(CyOc) segment, and eventually, three peaks (a−c) around 20−35 ppm and a peak (d) at 135 ppm can be reasonably assigned to cyclic methylene and olefinic carbons in the poly(CyOc) segment, respectively. The complete agreement of chemical shifts of the signals (e−g) due to the poly(PA) segment in the copolymer with those of the peaks (a−c) in the homopolymer of PA clearly reveals the formation of a block copolymer. In other words, one-shot feeding block copolymerization of CyOc with PA is possible. It is quite reasonable to assume that the resulting poly(CyOc) segment possesses cis geometrical structure because the Rh-catalyzed polymerization of acetylenes proceeds via the insertion mechanism,[3,8] and because the cis-to-trans isomerization of cyclooctene derivatives requires photoirradiation.[9] The well resolved ^{13}C resonances with very narrow half-height line width also supports the excellent degree of cis-stereoregulation of the CyOc polymerization.

In general, polymers from monosubstituted acetylenes are thermally unstable in comparison with those from disubstituted ones, and with *cis*-polymers, cis-to-trans irreversible isomerization readily takes place by heating. However, TGA and DSC measurements[7] manifested good thermal properties of poly(CyOc). For example, in TGA, poly(PA) exhibited an onset temperature of weight loss (T_0) at 300 °C in nitrogen. On the contrary, poly(CyOc) showed no weight loss up to 360 °C. The DSC curve of poly(PA) showed a large exothermic peak around 150 °C corresponding to the irreversible cis-to-trans isomerization, while such an evident peak was not detected for poly(CyOc). Poly(CyOc), thus, possesses higher thermal stability than poly(PA) and, below T_0, does not isomerize by thermal stimulation.

In summary, we have demonstrated that catalysts based on late transition metals such as Ni, Pd, and Rh efficiently polymerize cyclooctyne, a strained cyclic acetylene, which leads to the formation of a thermally stable, substituted polyacetylene having excellent cis stereoregularity. Copolymerizations with a wide variety of monomers including dienes, norbornenes, allenes, isonitriles, and so forth are currently in progress.

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Supporting Information Available: Figures showing IR spectra of CyOc and poly(CyOc), the ^1H NMR spectrum of poly(CyOc-*co*-PA) (sample from run 3, Table 2) in C_6D_6, and DSC curves of poly(CyOc) and poly(PA). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(5) A typical procedure of polymerization (run 8 of Table 1) is as follows: A 25-mL Schlenk tube was charged with 23 mg (0.050 mmol) of $[(nbd)RhCl]_2$ and 0.50 mL of distilled toluene. A 0.50 mL of monomer solution (2.0 M) in toluene was added to the catalyst solution with a syringe. After polymerization for 24 h at 30 °C, the reaction mixture was poured into an excess of methanol, and the polymer was corrected by filtration. The product was dried under vacuum for 24 h.

(6) Polymerization rate of PA can be reduced by adding PPh_3 when the polymerization is conducted with Rh catalysts. See: Kanki, K.; Misumi, Y.; Masuda, T. *Macromolecules* **1999**, *32*, 2384−2386.

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