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Homo- and copolymerizations of 3-(*N*-carbazolyl)-1-propyne and its homologues by Mo and W catalysts

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SUMMARY

3-(N-Carbazolyl)-1-propyne polymerized with $MoCl_5$- and WCl_6-based catalysts to produce a polymer in high yields. The $MoCl_5$ and $MoCl_5$–*n*-Bu_4Sn catalysts were the most effective (the systems solidified immediately after initiation of polymerization with these catalysts). The product polymer was a yellow solid insoluble in any solvent. Copolymerization of the present monomer with *tert*-butylacetylene by $MoCl_5$–*n*-Bu_4Sn produced a copolymer; it had a high molecular weight (M_w 350,000), completely dissolved in toluene, $CHCl_3$ etc, and formed a free-standing film by solution casting. ω-N-Carbazolyl-1-hexyne and -1-octyne produced toluene-insoluble polymers with WCl_6–Ph_4Sn.

INTRODUCTION

Polymers having carbazolyl groups such as poly(N-vinyl carbazole) are known to show interesting properties such as photoconductivity. The syntheses of high molecular weight polyacetylenes containing nitrogen, however, have been rather difficult because the basic nitrogen often inactivates transition metal catalysts (1). Thus, to our knowledge, the carbazole-containing acetylenes whose polymerizations have been examined are restricted to a few examples as follows: polymerization of N-carbazolylacetylene (**1**) with $Fe(acac)_3$-Et_3Al (2) and of 3-(N-carbazolyl)-1-propyne (**2**) with $Ti(OBu)_4$-Et_3Al and $WOCl_4$-Ph_4Sn (3) both of which only produce insoluble polymers and/or oligomers. Further, synthesis and photoconductivity of poly[bis(N-carbazolyl)-*n*-hexyl dipropargylmalonate] has recently been reported (4).

In the present study, we investigated the polymerization of 3-(N-carbazolyl)-1-propyne (**2**) with various Mo and W catalysts. Further, copolymerizations with other substituted acetylenes were examined to obtain soluble polyacetylenes with carbazolyl moieties.

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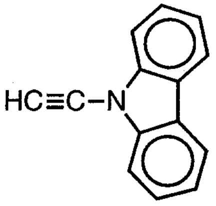

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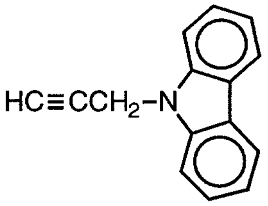

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EXPERIMENTAL

3-(N-Carbazolyl)-1-propyne was synthesized with reference to the literature method (5); the reaction, however, was carried out not in liquid ammonia but in an organic solvent: A 1-L, three-necked flask was equipped with a pressure-equalized dropping funnel, a reflux condenser and a magnetic stirring bar, and was then flushed with dry nitrogen. Sodium hydride (10.1 g, 0.25 mol, 60% in paraffin) was placed in the flask and the protecting paraffin was removed by washing with benzene. After the addition of benzene (ca. 600 ml) solution of carbazole (35.1 g, 0.21 mol), dimethyl sulfoxide (50-100 ml) was added dropwise at room temperature, and the mixture was stirred for 30 min. Then, propargyl bromide (25 g, 0.21 mol) was added gradually; carbazole was consumed completely in 3 h below 60 °C. After decomposition of sodium hydride with water, the benzene solution of 3-(N-carbazolyl)-1-propyne was washed with water, and the benzene was evaporated. The crude product was purified by a flush column chromatography with a toluene/hexane mixture (1:1 volume ratio) (R_f value: product 0.39, carbazole 0.21). Yield 70%; purity 98% (HPLC). Other acetylenes having a carbazolyl group was synthesized in the same way.

Transition metal compounds and organometallic cocatalysts were used as received. Polymerizations were carried out under dry nitrogen. The polymerization mixture was poured into a large amount of methanol to isolate the formed polymer. Monomer conversions were determined by HPLC (eluent: toluene/*n*-hexane (1:1) mixed solvent, column: silica gel 50 cm). Polymer yields were determined by gravimetry. Molecular weights of copolymers were measured by GPC (eluent: $CHCl_3$, columns: Shodex A805, A806, A807, a polystyrene calibration). IR and reflection spectra were recorded with Shimadzu IR435 and Shimadzu UV2100 spectrophotometers, respectively. Thermogravimetric analyses (TGA) were conducted with a Shimadzu 20B thermal analyzer (in air, heating rate 10°C/min). Other analyses were performed as described elsewhere (6).

RESULTS AND DISCUSSION

Polymerization of 3-(N-Carbazolyl)-1-propyne

Polymerization of 3-(N-carbazolyl)-1-propyne was studied by using Mo and W catalysts (Table I). The $MoCl_5$- and WCl_6-based catalysts achieved very high monomer conversions, and polymers were formed in high yields which virtually agreed with the monomer conversions. Especially, the catalytic activities of $MoCl_5$ alone and $MoCl_5$–*n*-Bu_4Sn were so high that the polymerization mixtures solidified immediately after initiation of the polymerization under the conditions shown in Table I. A possible reason why the monomer was not consumed quantitatively is that the polymerization mixtures were heterogeneous. On the other hand, the polymerization mixture using WCl_6-based catalysts did not solidify, which suggests that the polymers produced by $MoCl_5$-based catalysts have higher molecular weights, although the molecular weights cannot be determined because the polymers are insoluble in any solvent.

Table I
Polymerization of 3-(N-carbazolyl)-1-propyne
by Mo and W catalysts[a]

Catalyst	Solvent	Monomer convn,%	Polymer[b] yield,%
$MoCl_5$	toluene	88	80
$MoCl_5$–*n*-Bu_4Sn	toluene	88	84
$Mo(CO)_6$–hv	CCl_4	19	2
WCl_6	toluene	100	75
WCl_6–*n*-Bu_4Sn	toluene	91	88
$W(CO)_6$–hv	CCl_4	59	27

[a] Polymerized at 30 °C for 3 h; $[M]_0 = 0.50$ M, [Cat] = [*n*-Bu_4Sn] = 20 mM, $[Mo(CO)_6]$ = 10mM.
[b] Methanol-insoluble product.

Solvent effects on the polymerization of 3-(N-carbazolyl)-1-propyne were examined by using $MoCl_5$–*n*-Bu_4Sn (1:1) which proved to be the most effective catalyst (Table II). Polymers were obtained in high yields in chlorobenzene and anisole as well as in toluene. Polymers were produced in good yields even in more polar methyl benzoate and acetophenone. Considering that most substituted acetylenes cannot form polymers in these solvents, this monomer proves to have very high polymerizability. This high reactivity may be correlated with the relatively low basicity of the nitrogen atom conjugated with carbazole ring and with the moderate steric hindrance of the carbazolylmethyl group. The low polymer yield in CCl_4 is attributable to the low solubility of the monomer in CCl_4.

Table II
Solvent Effects on the Polymerization of 3-(N-Carbazolyl)-1-propyne by $MoCl_5$-*n*-Bu_4Sn (1:1)[a]

Catalyst	Monomer convn,%	Polymer[b] yield,%
toluene	88	80
PhCl	100	86
PhOMe	100	88
$PhCO_2Me$	97	73
PhCOMe	93	55
CCl_4	61	41

[a] Polymerized at 30 °C for 3 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM.
[b] Methanol-insoluble product.

The $MoCl_5$–*n*-Bu_4Sn catalyst produced poly[3-(N-carbazolyl)-1-propyne] in good yields in the temperature range -30 to 60 °C (Fig. 1). Virtually quantitative is the polymer yield (>90%) at 0 °C. Methanol-soluble linear oligomers formed to some extent at -30 and 60 °C.

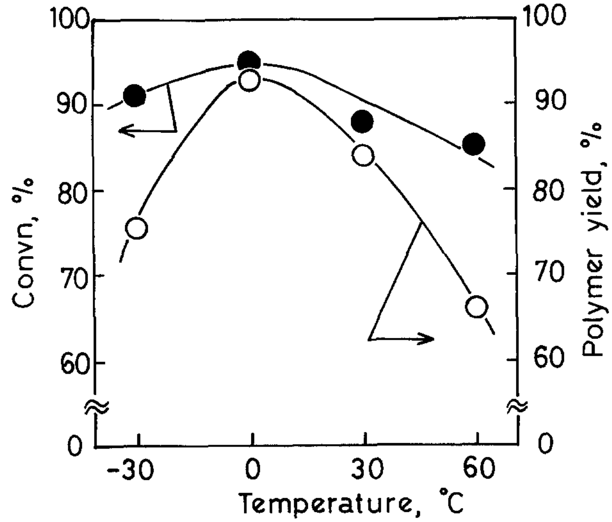

Figure 1. Temperature effect on the polymerization of 3-(N-carbazolyl)-1-propyne ($MoCl_5$-*n*-Bu_4Sn (1:1), in toluene, 3 h, $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM)

Structure and Properties of Poly[3-(N-carbazolyl)-1-propyne]

The structure and properties of poly[3-(N-carbazolyl)-1-propyne] did not depend on the catalyst system. The data described below have been obtained with the polymer sample formed with $MoCl_5$-*n*-Bu_4Sn catalyst.

The elemental analysis data of the polymer agreed well with their calculated values; Calcd for $(C_{15}H_{11}N)_n$: C 87.8%, H5.4%, N6.8%, Found: C 87.2%, H 5.3%, N 6.7%. Fig. 2 exhibits the IR and ^{13}C CP/MAS spectra of poly[3-(N-carbazolyl)-1-propyne]. Absorptions characteristic of =C-H (3000 cm^{-1}), carbazole ring (1600–1500 and 750 cm^{-1}), and aromatic tertiary amine (1350 cm^{-1}) are seen in the IR spectrum (KBr pellet). This spectrum shows no absorptions due to ≡C–H and C≡C which were observed in the IR spectrum of the monomer. The ^{13}C CP/MAS NMR spectrum exhibits a signal due to the methylene carbon (43 ppm) and those of the carbazole ring and the main chain (109, 120, and 140 ppm). The spectrum showed no signals due to the acetylenic carbons (72 and 78 ppm) observed in the monomer. It is concluded from these data that this polymer possesses alternating double bonds in the main chain.

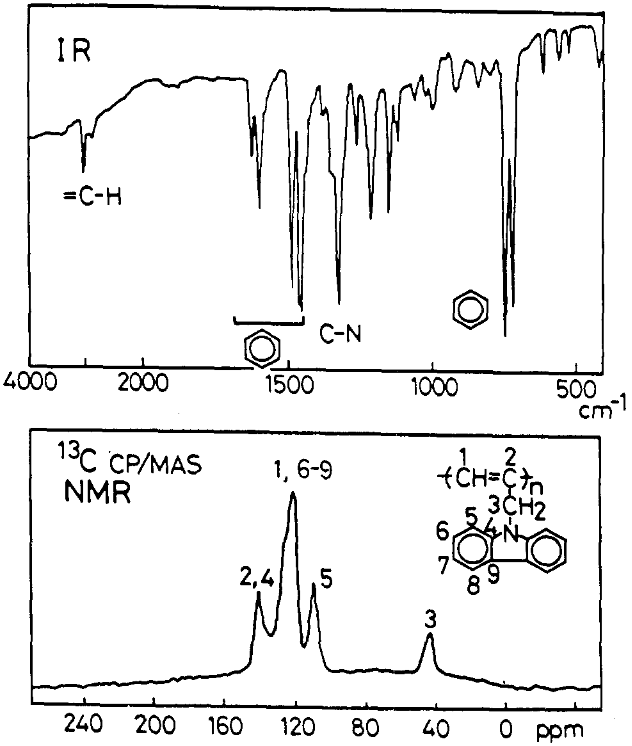

Figure 2. IR and ^{13}C CP/MAS NMR spectra of poly[3-(N-carbazolyl)-1-propyne]

Poly[3-(N-carbazolyl)-1-propyne] is a yellow solid, which did not dissolve in any solvent such as aromatic hydrocarbons, halogen-containing solvents, H_2SO_4, and HNO_3. The fairly good solubility of the polymer obtained with $Ti(OBu)_4$-Et_3Al seems due to its relatively low molecular weight (M_n 6×10^4) (3). The onset temperature of weight loss of poly[3-(N-carbazolyl)-1-propyne] in air was 260 °C, which means that this polymer is relatively stable among substituted polyacetylenes. The softening point of the polymer was 250 °C. The X-ray diffraction showed broad peaks at $2\theta = 20.2°$ ($\Delta 2\theta / 2\theta = 0.16$) and 23.3° (0.12). The ratios of half-height width to diffraction angle ($\Delta 2\theta / 2\theta$) indicate that poly[3-(N-carbazolyl)-1-propyne] is amorphous. The absorption cut-off in the reflection spectrum of the polymer was ca. 500 nm, which agrees with its yellow color.

Copolymerization with Other Substituted Acetylenes

In order to synthesize soluble polyacetylenes having carbazolyl groups, copolymerizations of 3-(N-carbazolyl)-1-propyne (M_1) with various substituted acetylenes were attempted. *tert*-Butylacetylene (7), *o*-(trimethylsilyl)phenylacetylene (6), and 1-chloro-1-octyne (8) were examined as comonomers (M_2) since they form high molecular weight polymers in the presence of Mo catalysts. Copolymerizations were carried out in toluene at 0 °C, $[M_1] = 0.10$ M, $[M_2] = 0.90$ M, and $[MoCl_5] = [n\text{-}Bu_4Sn] = 20$ mM.

The product of the copolymerization with *tert*-butylacetylene had the following features:

1) the GPC curve is unimodal
2) it is totally soluble in toluene, $CHCl_3$, THF etc.
3) it exhibits absorptions characteristic of both 3-(N-carbazolyl)-1-propyne and *tert*-butylacetylene units in the IR spectrum.

Thus, the copolymerization product is concluded to be a copolymer. The copolymer yield was 90 wt%, and the weight- and number-average molecular weights were 35×10^4 and 21×10^4, respectively. This copolymer provided a free-standing film on solution casting. On the other hand, the copolymerization product with *o*-(trimethylsilyl)phenylacetylene showed a bimodal GPC curve, and the product with 1-chloro-1-octyne was partly insoluble in toluene. These results mean that uniform copolymers have not been formed from these two comonomers, which is attributable to the fact that 3-(N-carbazolyl)-1-propyne is much more reactive than these comonomers.

Polymerization of Other Acetylenes Having a Carbazolyl Group

Polymerizations of ω-(N-carbazolyl)-1-hexyne and -1-octyne ($HC{\equiv}C(CH_2)_nCz$; Cz: carbazolyl group, n = 4 and 6) were examined in order to obtain soluble polyacetylenes. While $MoCl_5$–Ph_4Sn formed only oligomers, WCl_6–Ph_4Sn produced toluene-insoluble polymers (yield 60%) and oligomers. These monomers tended to form oligomers compared with 3-(N-carbazolyl)-1-propyne, which is probably because of smaller steric hindrances of the substituents as in linear 1-alkynes. Further, neither $HC{\equiv}CCH_2NPh_2$ nor $HC{\equiv}CCH_2NMe_2$ give a methanol-insoluble polymer with $MoCl_5$– and WCl_6–based catalysts (9), which may be attributed to the higher basicity of their nitrogen atoms. Thus it is quite interesting that 3-(N-carbazolyl)-1-propyne polymerizes in high yield. Soluble high molecular weight polymers will be synthesized by introducing a long alkyl chain onto the carbazolyl ring of 3-(N-carbazolyl)-1-propyne.

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