Pergamon

Tetrahedron Letters 42 (2001) 1437–1439

TETRAHEDRON
LETTERS

An unprecedented cation radical chain Diels–Alder polymerization leading to novel carbazole polymers

Nathan L. Bauld* and Yeonsuk Roh

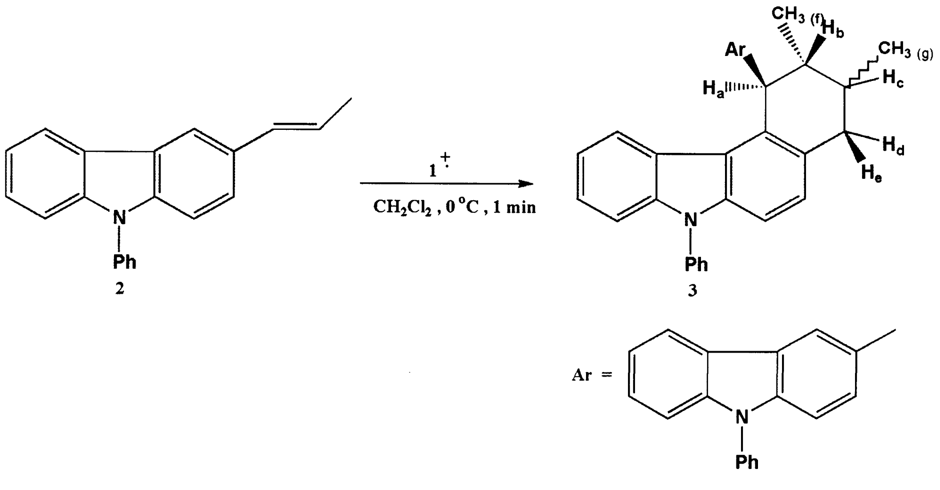
Department of Chemistry and Biochemistry, The University of Texas, Austin, TX 78712, USA

Received 25 September 2000; accepted 11 December 2000

Abstract—The polymerization of 3,6-bis(*trans*-1′-propenyl)-*N*-phenylcarbazole in the presence of tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{+\bullet}$) leads to soluble, high molecular weight, thermally stable cycloaddition polymers containing carbazole units in the main polymer chain. The reaction appears to proceed via a highly efficient cation radical chain mechanism which circumvents the usual hole transfer step of the propagation cycle. This polymerization represents the first observation of direct cation radical Diels–Alder cycloaddition polymerization. © 2001 Elsevier Science Ltd. All rights reserved.

Cation radical chain cycloaddition polymerizations have only recently been observed.[1] The examples thus far reported exclusively involve cyclobutanation as the initial cycloaddition mode for monomer attachment. We now wish to report the first example of a highly efficient and direct cation radical chain Diels–Alder polymerization. This polymerization is of special interest in that one of the double bonds of the conjugated diene system is part of an aromatic ring, and the resulting polymers contain carbazole residues in the main polymer chain, a type of polymer which is of particular interest for applications in optoelectronic devices.[2]

The chemistry of a monofunctional analogue, 3-(*trans*-1′-propenyl)-*N*-phenylcarbazole (**2**),[3] provides the necessary foundation for understanding the polymerization mechanism. When **2** was treated in dichloromethane solution at 0°C with $\mathbf{1}^{+\bullet}$ (15 mol%) for 1 minute, followed by quenching with excess saturated methanolic potassium carbonate, aqueous workup and column chromatography, a 34% yield of the mixture of diastereoisomeric dimers (**3**) was obtained (Scheme 1). The structure of these dimers was established by ^{1}H and ^{13}C NMR and H–H correlation spectra, as well as by LRMS and HRMS.[4] The same dimer mixture was obtained in 43% yield when the reaction was carried



Scheme 1.

Keywords: cation radical; polymerization; carbazole; chain mechanism; Diels–Alder.

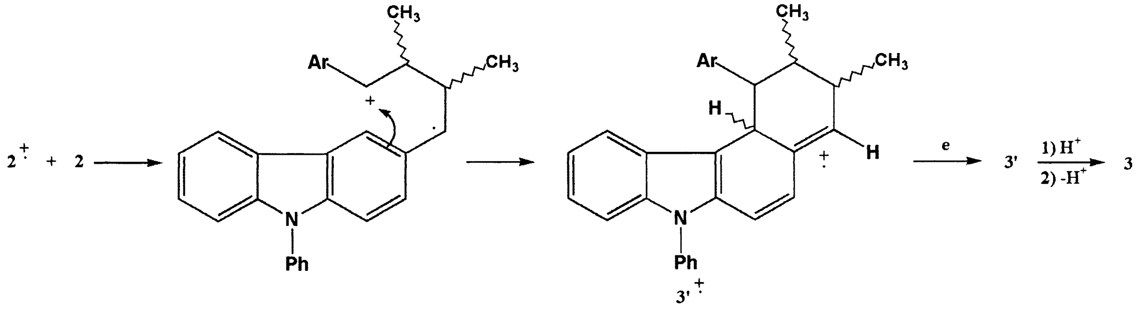
* Corresponding author.

0040-4039/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(00)02301-7

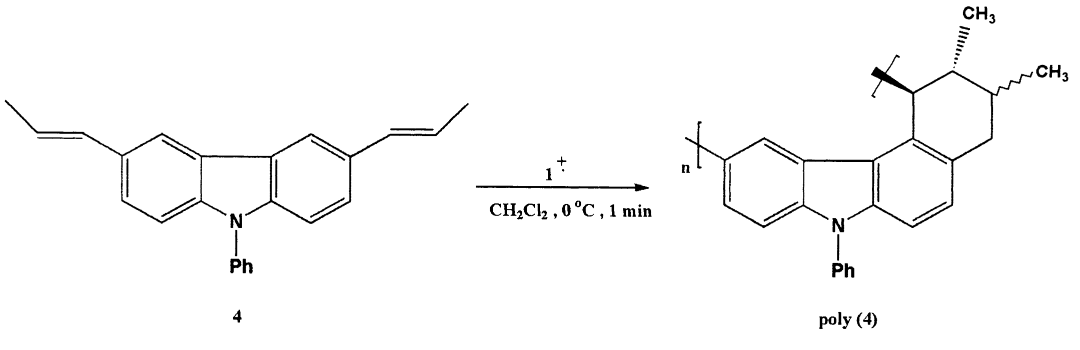
out in the presence of 2,6-di-*tert*-butylpyridine, thus precluding the possibility of an acid catalyzed or other carbocation-mediated process.[5] Several close precedents already exist for analogous reactions in which, in an overall sense, cation radical Diels–Alder reactions involving addition to a double bond of an aromatic ring are observed.[6] These reactions are generally considered to be stepwise in nature, proceeding via distonic cation radical intermediates which subsequently cyclize to the *ortho* position of the aromatic ring (Scheme 2). The aromaticity of the ring is then restored via processes which are not yet well defined.

We then synthesized and polymerized 3,6-bis(*trans*-1′-propenyl)-*N*-phenylcarbazole (**4**; Scheme 3).[7] When this monomer was treated in dichloromethane solution at 0°C with $\mathbf{1}^{+\bullet}$ (15 mol%) polymerization occurred rapidly. Quenching with methanolic potassium carbonate followed by a typical two phase water/dichloromethane workup gave a glassy polymer which was highly soluble in dichloromethane and other organic solvents. This polymer was found to have M_W 106 200 (PDI 3.1). The ^{1}H NMR absorptions of the polymer in $CDCl_3$ solution were unusually broad, so that the NMR spectrum was examined at 50°C. The polymer has no detectable traces of absorptions (methyl and olefinic) corresponding to unreacted propenyl end groups, indicating that both propenyl groups of the monomer have reacted essentially completely. Cycloaddition polymerization is thus indicated, since linear polymerization of a difunctional monomer would necessarily generate an insoluble, network polymer. In the aliphatic region, the chemical shifts of the NMR absorptions of the polymer correspond very closely with those of **3**.[8] When the polymerization of **4** was carried out in the presence of 10 mol% of **2** (to cap the polymer at a lower molecular weight), the resulting polymer was found to have a weight average molecular weight of 62 100, and the NMR spectrum could then be conveniently observed at ambient temperatures. Finally, even when the polymerization process was carried out with a 2:1 ratio of **2**:**4**, an 85% yield of oligomers (average nonamers) was formed, providing further evidence that the polymerization is indeed occurring via a chain growth process. The proton NMR spectrum of these oligomers is virtually identical to that of the high molecular weight polymer, except for line width. In addition to these oligomers, a small amount (10% yield) of the 2:1 adduct (**2**:**4**) was isolated from this mixture, and the NMR spectrum of this ‘trimer’ proved to be virtually identical in the aliphatic region to that of the dimer **3**.

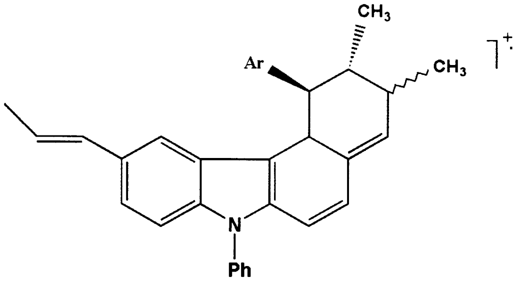
It is significant that, notwithstanding the rather modest yields of dimers which are obtained in the reaction of the monofunctional analogue **2**, the polymerization of **4** is extremely rapid and highly efficient in generating Diels–Alder type linkages. It is considered to be a key to the efficiency of cation radical cycloaddition polymerizations that the hole transfer which is required for the neutralization of the adduct cation radicals and which, in the case of monofunctional substrates, is required to be intermolecular, can be intramolecular and therefore potentially much faster in the case of difunctional molecules. The special efficiency observed in the present polymerizations appears to derive from the circumstance that even intramolecular hole transfer is circumvented, because the adduct cation radical, as it



Scheme 2.



Scheme 3.



Scheme 4.

is initially formed, is presumably already delocalized, in significant part, upon the reactive propenyl moiety (Scheme 4). Propagation of the chain by reaction at this propenyl moiety is therefore feasible.

Acknowledgements

The authors wish to acknowledge the Robert A. Welch Foundation (F-149) for support of this work.

References

1. (a) Bauld, N. L.; Aplin, J. T.; Yueh, W.; Sarker, H.; Bellville, D. *Macromolecules* **1996**, *29*, 3661–3662; (b) Bauld, N. L.; Aplin, J. T.; Yueh, W.; Endo, S. *J. Phys. Org. Chem.* **1998**, *11*, 825–830; (c) Bauld, N. L.; Gao, D.; Aplin, J. T. *J. Phys. Org. Chem.* **1999**, *12*, 808–818; (d) Bauld, N. L.; Gao, D. *Polym. Int.* **2000**, *49*, 253–259.
2. (a) Biswas, M.; Das, S. K. *Polymer* **1982**, *23*, 1713–1726; (b) Wada, T.; Sasaba, H. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1993**, *34*, 763–764.
3. Prepared from *N*-phenylcarbazole by (1) monoacylation with propionyl chloride/$AlCl_3$ (59%), (2) reduction with sodium borohydride in ethanol/THF (99%), and (3) dehydration by phosphorus oxytrichloride/pyridine (91%).
4. The chemical shift assignments for the two major dimers were derived from H–H COSY spectra. Only the crucial assignments for the protons attached to saturated carbon are given here: Isomer A: δ 4.63 (H_a, d, $J=6.2$), 2.94 (H_e, ddd, $J=6.8$, 5.0, 1.8), 2.34 (H_b, dq, $J=6.6$, 6.8), 1.92 (H_d, m), 1.80 (H_c, tq, $J=7.4$, 6.6), 1.43 (H_f, d, $J=6.8$), 1.03 (H_g, d, $J=6.0$); Isomer B: δ 4.78 (H_a, d, $J=4.2$), 3.4 (H_e, ddd, $J=6.5$, 4.8, 1.8), 2.79 (H_b, dq, $J=4.2$, 2.6), 1.92 (H_d, m), 1.70 (H_c, tq, $J=7.4$, 5.0), 1.21 (H_f, d, $J=7.0$), 1.03 (H_g, d, $J=6.0$). The aromatic protons of both isomers absorbed in the range of δ 7.1–8.12 and were very similar to those of *N*-phenylcarbazole except that the C_4 proton of the aryl substituent (Ar in Scheme 1) is a singlet, and the C_4 proton of the other carbazole ring is missing.
5. Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993–7994.
6. (a) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 608–609; (b) Kadota, S.; Tsubono, K.; Makino, K.; Takeshita, M.; Kikuchi, T. *Tetrahedron Lett.* **1987**, *28*, 2857–2860; (c) Wilson, R. M.; Dietz, J. G.; Shepherd, T. A.; Ho, D. M.; Schnapp, K. A.; Elder, R. C.; Watkins, J. W.; Geraci, L. S.; Campana, C. F. *J. Am. Chem. Soc.* **1989**, *111*, 1749–1754.
7. The synthesis of the bis(propenyl) compound proceeded in the same manner as the monopropenyl derivative, i.e. bispropionylation (84%), reduction (96%), and dehydration (75%).
8. ^1H NMR (500 MHz, $CDCl_3$, 50°C) δ 4.8–4.6 (br), 3.5–3.3 (br), 2.9–2.6 (br), 2.3–2.2 (br), 1.9–1.6 (br), 1.4–0.9 (br). The chemical shifts of these absorptions and their approximate areas correspond very well with those observed in the spectrum of the mixture of four diastereoisomers of **3** except that the absorptions of the polymer are broad.