Communications to the Editor

Synthesis of Novel Thermotropic Liquid Crystalline Poly(2,3-quinoxaline)s

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Much attention has been paid to the synthesis of liquid crystalline polymers. In general, thermotropic liquid crystalline polymers are classified into three types: (a) main-chain LC polymer, (b) side-chain LC polymer, and (c) rigid-rod LC polymer (Figure 1).[1] LC polymers of types a and b possess liquid crystallinity due to the mesogenic properties of their monomer units. In LC polymers of type c, on the other hand, the mesogenic rigidity is derived from the rodlike structure of the main chain which is formed with the progress of polymerization and is balanced with surrounding flexible side chains of the polymer. Thus, the liquid crystallinity of LC polymers of type c does not originate in the structure of the monomer but in the polymer structure constructed. Dependency of thermal behavior of LC polymers on the molecular weight is a subject of interest and has been studied using a side-chain LC polymer.[2] In the synthesis of the rigid-rod LC polymer, the rigid-rod-like structure grows with the progress of polymerization. The polymers of low degree of polymerization (DP) would not have enough backbone rigidity to reveal liquid crystallinity. At a certain critical DP, the rigid-rod polymer would begin to have enough rigidity to exhibit thermotropic liquid crystalline nature. However, such dependency of phase behavior of rigid-rod LC polymer on DP has not so far reported, because the known rigid-rod polymers such as polypeptide,[1] poly(isocyanate),[3] cellulose,[4] and polyester[5] were not easily accessible with control of DP.

Recently, we described a new living polymerization of 1,2-diisocyanoarenes catalyzed by methylpalladium(II) complex giving poly(2,3-quinoxaline)s, which have helical structures.[6,7] Furthermore, a screw-sense selective polymerization of 1,2-diisocyanoarenes was successfully achieved by chiral palladium catalysts having helical conformations.[7] Empirical energy and theoretical CD calculations supported that the main-chain structure of the poly(2,3-quinoxaline) is composed of a rigid helix.[8] In the present paper, we report that the polymerization of 1,2-diisocyanoarenes with varying alkoxymethyl side chains provides novel thermotropic rigid-rod LC polymers. It is remarked that the liquid crystallinity was revealed on balancing of the rigidity of the poly(2,3-quinoxaline) backbone with the flexibility due to the side chains.

4,5-Bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanoarenes (**6a–c**) were prepared according to Scheme I. (Tetrabromobenzo)-2,1,3-thiadiazole (**1**), prepared by stepwise bromination of (5,6-dimethylbenzo)-2,1,3-thiadiazole,[9] was treated with the corresponding alkoxymagnesium(II) and then with methylzinc chloride in the presence of [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) chloride to afford **3a–c**. Reduction into *o*-phenylenediamine derivatives **4a–c**, formylation with acetic formic anhydride, and dehydration with trichloromethyl chloroformate furnished the corresponding 4,5-bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanoarenes (**6a–c**) in satisfactory overall yield from **1** (45–55%).

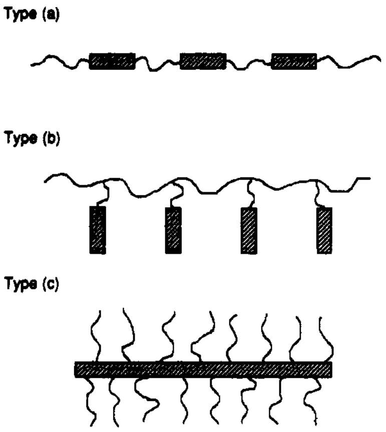
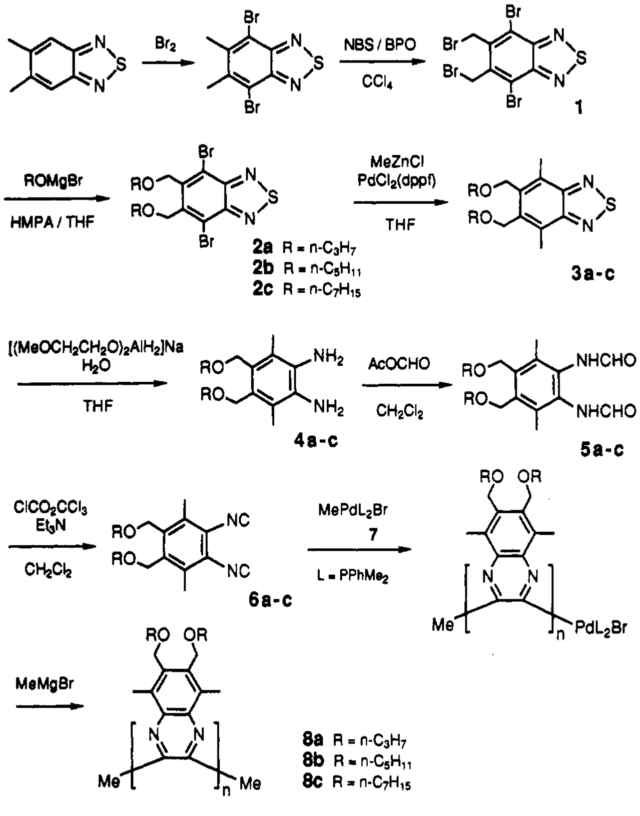


Figure 1.

Scheme I



Polymerization of 4,5-bis(alkoxymethyl)-3,6-dimethyl-1,2-diisocyanoarenes (**6**) thus prepared was catalyzed by methylpalladium(II) complex in THF. After the monomer **6** was completely consumed, the propagating quinoxalinylpalladium(II) moiety was quenched by a coupling reaction with methylmagnesium bromide to give poly-

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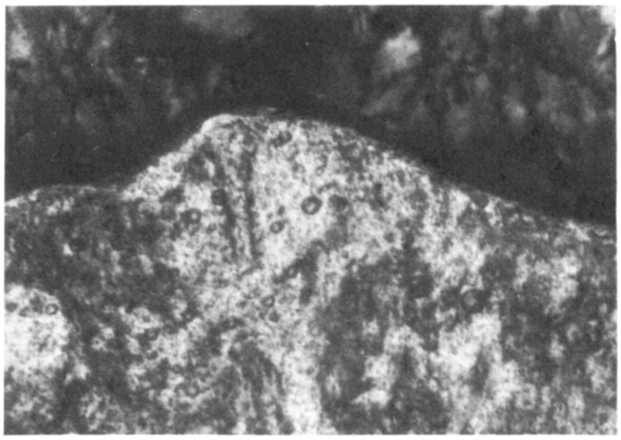
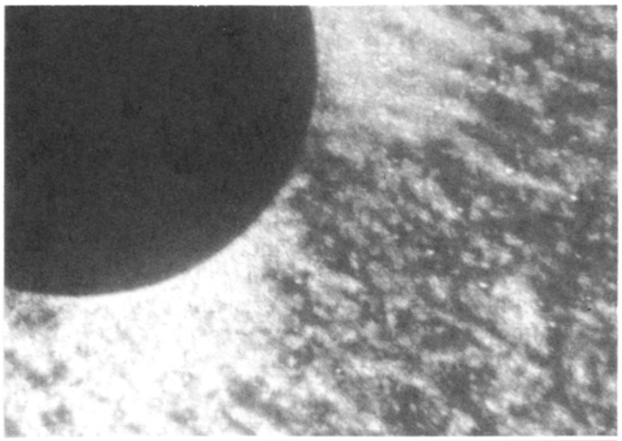
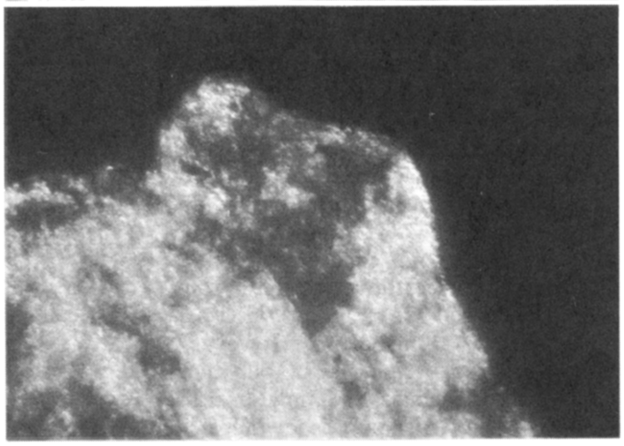


(a) **8a**-30 at 150 °C (x 200)



(b) **8b**-50 at 130 °C (x 200)



(c) **8c**-100 at 120 °C (x 200)

Figure 2.

(2,3-quinoxaline)s **8** having various alkoxymethyl side chains on the 6- and 7-positions in high yield (Table I). In accord with the living polymerization, the molecular weights were controlled by the feeding ratio of the monomer to the palladium catalyst (**6**/**7**) and the molecular weight distribution were very narrow. The phase behavior of the poly(2,3-quinoxaline)s was examined by an optical polarized microscope and analyzed in terms of the degree of polymerization (Table I). Mesophases were observed in the temperature range higher than 120 °C, although the exact phases were not assigned. Noteworthy was that only the poly(2,3-quinoxaline)s of sufficiently high DP exhibited the mesophase, whereas poly(2,3-quinoxaline)s of low molecular weight did not pass any mesophase at all. In the case of poly(2,3-quinoxaline) **8a** having (propyloxy)methyl side chains, the critical point of DP for the appearance of mesophase exists between 20 and 30. The DP range for the appearance of liquid crystalline nature depends upon the length of alkoxymethyl side chains. A higher DP was required for the poly(2,3-quinoxaline) having a longer side chain to display liquid crystallinity.

Table I
Polymerization of 6 and Phase Behavior of Poly(2,3-quinoxaline)s 8

	reaction conditions				yield,	GPC		liquid
run	6	6/7	temp	sample	%	M_n	M_w/M_n	crystallinity[a]
1	**6a**	10	rt[b]	**8a**-10	98	2670	1.12	×
2		20	rt	**8a**-20	98	3540	1.12	×
3		30	rt	**8a**-30	87	7650	1.17	○
4		50	rt	**8a**-50	84	13410	1.23	○
5		70	rt	**8a**-70	84	20550	1.18	○
6		100	rt	**8a**-100	93	33100	1.22	○
7	**6b**	30	rt	**8b**-30	72	7500	1.09	×
8		50	rt	**8b**-50	67	13670	1.14	○
9		70	reflux	**8b**-70	73	19780	1.09	○
10		100	reflux	**8b**-100	99	31370	1.08	○
11	**6c**	30	reflux	**8c**-30	99	8140	1.11	×
12		40	reflux	**8c**-40	86	9750	1.19	×
13		50	reflux	**8c**-50	96	12410	1.14	×
14		70	reflux	**8c**-70	99	17120	1.12	○
15		100	reflux	**8c**-100	90	31360	1.16	○

[a] A sample marked ○ exhibited liquid crystallinity while a sample marked × did not pass mesophase. [b] rt = room temperature.

These findings may suggest that the helical backbone, which is built from 2,3-quinoxaline units, provides the rigid mesogenic segment of the LC polymer. In order to reveal liquid crystallinity, the rigidity due to the helical backbone of poly(2,3-quinoxaline)s is to be balanced by the flexibility of the polymer which depends on the length of the side chains. The poly(2,3-quinoxaline) of lower DP than the critical point could not exhibit the mesophase because of the insufficient rigidity. Figure 2 shows the optical textures of the poly(2,3-quinoxaline)s observed by microscope. Assignment of the exact phase of the liquid crystal is now undertaken.

References and Notes

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Registry No. 1, 144042-97-7; **6a**, 144042-98-8; **6a** (homopolymer), 144043-01-6; **6b**, 144042-99-9; **6b** (homopolymer), 144043-02-7; **6c**, 144043-00-5; **6c** (homopolymer), 144071-93-2; **8a**, 144043-03-8; **8b**, 144071-94-3; **8c**, 144071-95-4; $(PPhMe_2)_2Pd(Me)Br$, 42745-00-6.