Macromolecules **2001,** *34,* 4308−4313

Articles

Kinetic Study of the Knoevenagel Condensation Applied to the Synthesis of Poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)]s

Valérie Boucard*

Laboratoire de Recherches sur les Macromolécules, Institut Galilée, Université Paris 13,
99 avenue J. B. Clément, 93430 Villetaneuse, France

Received December 29, 2000; Revised Manuscript Received March 27, 2001

ABSTRACT: The Knoevenagel condensation has been applied to the synthesis of [bicarbazolylene-*alt*-phenylenebis(cyanovinylene)] copolymers and their model compounds. The kinetic study at 65 °C showed a very complex reaction: the apparent order was found to change with the modification of experimental conditions. In methanol the reaction rate is governed by the dissociation step of the active methylene compound (step 1 of the reaction mechanism). In THF/MeOH mixtures, the rate-determining step is a result of the relative rate ratio step 1/step 2. The influence of several dipolar interactions between the active methylene compounds, the aldehyde monomers, and the solvents used is discussed along with the effects of the polarity and the concentration of comonomers on reaction rates. More importantly, the possibility to control precisely the reaction rate via the appropriate choice of the dielectric constant of the initial medium is emphasized. Finally, the observed results obtained have been transposed to the synthesis of wholly THF-soluble conjugated copolymers, which can reach molecular weight equal to 25 000, in polystyrene equivalent.

Introduction

The Knoevenagel condensation reaction has been reported first in 1894.[1] Since then, systematic studies remain scarce in the literature.[2−7] In particular, Patai et al. have shown the complexity of the reaction.[6,8−11] The Knoevenagel condensation depends not only on the relative reactivity of reactants, the strength of the bases employed, and the nature of solvents and their dissociating powers but also on the importance of side reactions (Michael and Thorpe−Ziegler reactions).[12−14] Moreover, the apparent order changes with the experimental conditions. The difficulty to control all these parameters is probably the reason why the Knoevenagel condensation had been finally not widely employed and studied since 1960s.

In fact, the condensation reaction has been recently reused for the synthesis of new conducting materials, in particular by the Cambridge group for the synthesis of poly(phenylene cyanovinylene)s.[15] These materials have been shown to exhibit electroluminescence, that is, a light emission produced by the action of an electrical current.

Since the recent discovery of electroluminescence in poly(*p*-phenylenevinylene) (PPV),[16] a wide range of conjugated and semiconjugated polymers have been used as the active emissive layer in light-emitting diodes (LEDs).[17] We have previously reported results concerning multilayer organic diodes based on either poly(*N*-alkyl-3,6-carbazolylene)[18] (PCZ), a polymer with an all-carbazole skeleton or derivatives of the PCZ constituting dyads, i.e., bicarbazyl.[19,20] These LEDs display a bright blue light. Recently, we have studied the possibility to combine the advantages displayed by both the PPV and the PCZ into a unique polymeric structure. To this end, we have synthesized the poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)][21] (PCPV) by the Knoevenagel condensation. It was found that this alternating copolymer exhibits an internal charge transfer between the electron-donor carbazole subunits and the electron-acceptor cyanovinylene moieties that allows shifting the electroluminescence from blue to green.[22] Thus, by varying the nature of the cyanovinylene subunit, it is possible to modulate the electroluminescent color and to ameliorate the solubility of new bicarbazolylene materials.

But before going through the synthesis of this new family copolymers, an understanding of the Knoevenagel condensation reaction is needed. To this end, the kinetic of the synthesis of two model compounds of poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)]s and its application to the synthesis of a soluble conjugated copolymer were studied and reported here.

Results and Discussion

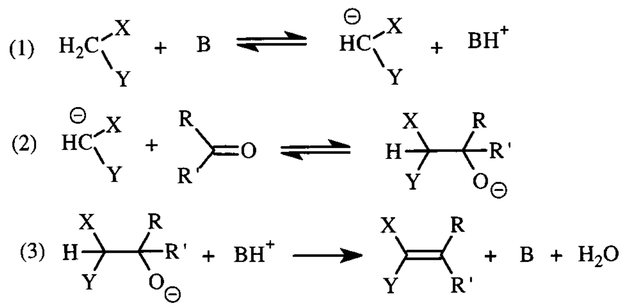
The Knoevenagel Condensation. Since 1896, the Knoevenagel condensation had been defined as the reaction between an aldehyde or ketone and any compound having an active methylene group, brought by an organic base or ammonia or their salts.[23] The activation of the methylene group is due to the direct attachment of one group such as nitro, cyano, or acyl, and in most cases two such groups are required to provide sufficient activation. The product obtained is an unsaturated compound.

---

* E-mail: vboucard@galilee.univ-paris13.fr.

10.1021/ma002233g CCC: $20.00

Scheme 1. Mechanism of the Knoevenagel Condensation



Although the Knoevenagel mechanism is the subject of some agreement (Scheme 1),[4,6,24,25] no direct proof concerning the intervention of the carbanion has been brought. Recently, we have found, by proton and carbon NMR, that the reaction intermediate formed in step 1 was not a carbanion but a partially ionized species in methanol. These results will be published later.

To understand the Knoevenagel reaction, we have examined the kinetics of the polycondensation reaction (Scheme 2). The synthesis of the monomer **1**[21] being carried out in three steps with many purification steps and an overall yield close to 55%, we have preferred to synthesize first a model compound of the copolymer. The simplest one would have been the product of the condensation between the *N*-ethylcarbazolecarboxaldehyde (**4**) and the phenylene–monoacetonitrile, but the compound obtained was too difficult to purify. Moreover, the results were not reproducible enough. Therefore, we have chosen to study the condensation of the *N*-ethylcarbazolecarboxaldehyde (**4**) and the *p*-phenylenediacetonitrile (**2**) catalyzed by the tetrabutylammonium hydroxide in refluxing methanol (Scheme 3) as the model reaction of the polycondensation. There are two condensations for this model reaction, the second one being faster than the first due to the fact that the macromolecular chains in the copolymer were exclusively ended by aldehyde functions.[21] Actually, as soon as the first acetonitrile function of **2** reacted with one aldehyde function of **1**, the second acetonitrile function reacted quickly with another molecule **1**. Thereby the kinetic study will give us information only about the slowest Knoevenagel condensation, i.e., the first one.

Kinetic Study of the Knoevenagel Condensation in Methanol at 65 °C. 1. Stoichiometric Conditions. In accordance with the paper by the Cambridge group,[15] we have chosen the tetrabutylammonium hydroxide as the basic catalyzer. Because this catalyzer is supply in solution with methanol, we have preferred first to study reactions in pure methanol. Moreover, condensations must be led in a refluxing solvent to avoid side reactions,[21] namely, the Thorpe–Ziegler condensation occurring with the acetonitile functions.[13,14] Unfortunately, due to these side reactions, the study of the effect of temperature on kinetics and determination of activation energies have been impossible. Thus, kinetics has been examined at only 65 °C.

To determine which one of the three steps of the mechanism (Scheme 1) governs the rate of the model reaction, we have undertaken a kinetic study of the condensation reaction between **2** and **4** with three different base concentrations (Figure 1). A graphic method has shown that the apparent order of the reaction was equal to 1 i.e., $-\mathrm{d}[\mathrm{CH_2CN}]/\mathrm{d}t = k'[\mathrm{CH_2CN}]$ or, after integration, $\ln([\mathrm{CH_2CN}]_0/[\mathrm{CH_2CN}]) = k't$ with k' the apparent rate constant (Figure 2). Otherwise, we have verified that the Knoevenagel condensation of **2** and **4** was complete and that there was no side reaction in these experimental conditions, as previously reported,[21] the yield of the recovered polymer obtained in 1 week reaching more than 99% for each base concentration.

The fact that the apparent order equals to 1 means that the first step of the mechanism is the step that determines the rate of the Knoevenagel condensation. Moreover, the slopes of the plots in Figure 2 are equal to the apparent constant rates which vary linearly with base concentrations. That suggests that the reaction is of one order with respect to the active methylene group **2**, as it is with respect to the base, which is regenerated at the end of reaction (Scheme 1, step 3). The same reaction is of zero order with the aldehyde **4**, namely, independent of its concentration and its nature. These results are in agreement with those by Patai,[6] who used different experimental conditions.

Actually, the first step of the mechanism is an acid–base reaction. In that case, the ionic strength and the dissociating power of solvents should influence the rate of the active methylene dissociation. Hence, we have tried to show the influence of the dielectric constant ϵ of the initial medium on the reaction rate. To this end, we have led the model reaction, at 65 °C to avoid side reactions,[21] in different solvent mixtures with various proportions: water/MeOH, iPrOH/MeOH, tBuOH/MeOH, and THF/MeOH. The resulting dielectric constant of the solvent mixtures $\epsilon_{\mathrm{mixture}}^{25\,°\mathrm{C}}$ could be calculated at 25 °C from values found in the literature according to the example of the following equation (for THF/MeOH mixtures):

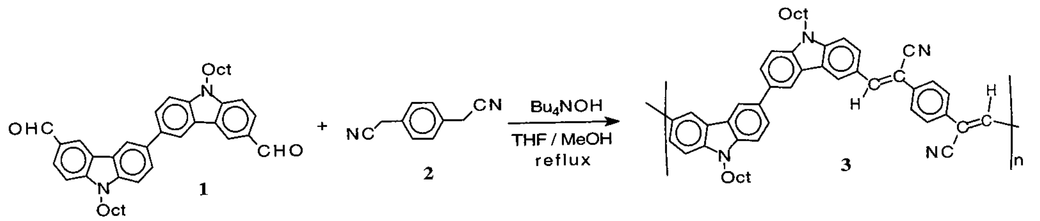
$$\epsilon_{\mathrm{mixture}}^{25\,°\mathrm{C}} = \epsilon_{\mathrm{MeOH}}^{25\,°\mathrm{C}}\Phi_{\mathrm{MeOH}} + \epsilon_{\mathrm{THF}}^{25\,°\mathrm{C}}\Phi_{\mathrm{THF}} \qquad (1)$$

where Φ_{MeOH} and Φ_{THF} represent the volume fraction of methanol and tetrahydrofuran in this mixture, respectively, and $\epsilon_{\mathrm{MeOH}}^{25\,°\mathrm{C}}$ and $\epsilon_{\mathrm{THF}}^{25\,°\mathrm{C}}$ are the dielectric constants of methanol and tetrahydrofuran, respectively. Generally, dielectric constant decreasing when the temperature increases, real dielectric constants of mixtures are then lower than the calculated ones. For solvent mixtures with low methanol concentration a modification of the apparent order of the reaction from one to two was observed. In fact, if the solvent mixtures are in adequate proportions, the apparent order of reaction should be equal to 1 and the apparent rate constants follow the Born and Kirkwood laws[26,27] (Figure 3). The observed straight lines follow the Born law as

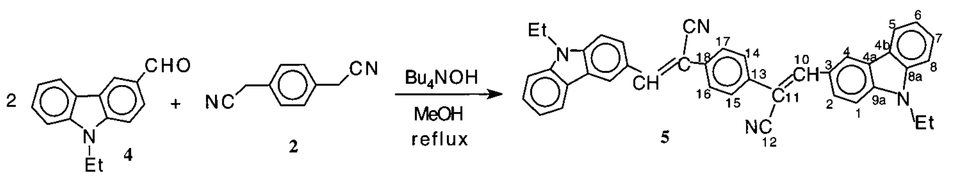
$$\ln k = \ln k_0 - \frac{Nze\mu}{RTr^2}\frac{1}{\epsilon} \qquad (2)$$

where k_0 represents the rate constant in medium with very high dielectric constant, N is the Avogadro number, e is the electron charge, μ is the local dipolar moment of the methylene compound (assuming equal to 4.5 D), R is the perfect gas constant, T is the temperature, and r indicates the minimal distance of reaction, namely, the necessary distance in order that the reaction occurs between the OH$^-$ base and the active methylene group. The r variation (Table 1), from 2.54 Å in the presence of THF to 1.33 Å with 2-propanol, shows that the presence of low dissociating molecules (lower dielectric

Scheme 2. Synthesis of Poly[bicarbazolylene-*alt*-*p*-phenylenebis(cyanovinylene)] (3) via the Knoevenagel Condensation



Scheme 3. Model Knoevenagel Condensation of *N*-Ethylcarbazolecarboxaldehyde (4) and *p*-Phenylenediacetonitrile (2)



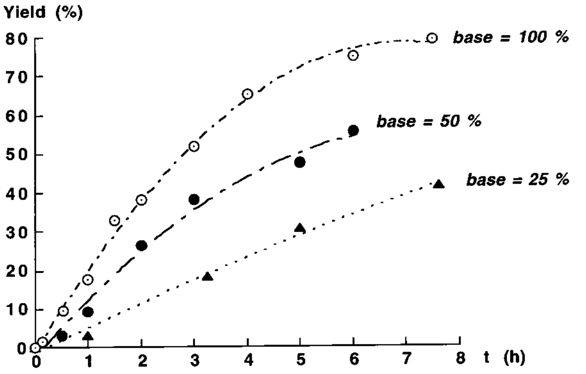


Figure 1. Knoevenagel condensation of **2** and **4** in stoichiometric conditions in methanol at 65 °C. “Base = 100%” means that there is as much moles of base as moles of initial acetonitrile function: $[CH_2CN]_0 = 0.06$ mol L^{-1}.

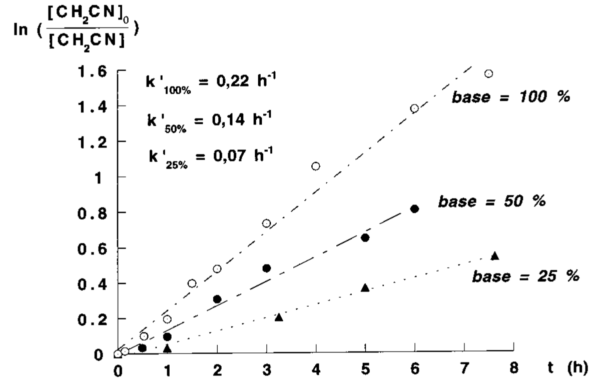


Figure 2. Apparent order is equal to 1 in the Knoevenagel condensation of **2** and **4** with stoichiometric conditions in pure methanol at 65 °C. “Base = 100%” means that there is as much moles of base as moles of initial acetonitrile function: $[CH_2CN]_0 = 0.06$ mol L^{-1}.

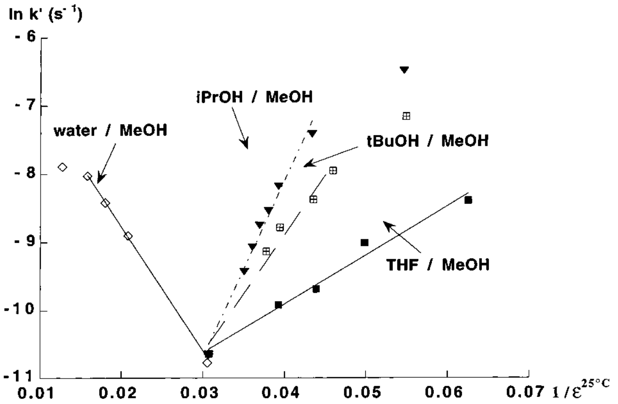


Figure 3. Dependence of the first-order apparent rate constant k' with the resulting calculated dielectric constant $\epsilon^{25°C}$ of THF/MeOH, tBuOH/MeOH, iPrOH/MeOH, and water/MeOH mixtures, in the case of the condensation between **2** and **4** at 65 °C. $\epsilon^{25°C}$ is calculated according to the example of eq 1. Time reactions = 1 h, $[base]_0/[CH_2CN]_0$ = 50%, and $[CH_2CN]_0 = 0.06$ mol L^{-1}.

Table 1. Dielectric Constants of Different Solvents and the Values of *r*, the Minimal Distance of the Knoevenagel Reaction, for Four Solvent/MeOH Mixtures ($\epsilon^{25°C}$ of Pure Methanol = 32.63) in the Case of the Condensation between 2 and 4 at 65 °C

solvent/MeOH mixtures	$\epsilon^{25°C}$ of pure solvent	*r* (Å)
water	78.5	1.59
iPrOH	18.3	1.33
tBuOH	10.9	1.63
THF	7.0	2.54

constant) makes it difficult for the OH$^-$ to get close to the methylene group. This is probably due to a smaller polarization of **2** by the solvent mixture.

It is likely that the attack of a given ion on a polar molecule has occurred preferentially at the opposite sign pole. That means the electrostatic energy will support the reaction, and consequently the slopes of Born law plots will be positive. However, the steric hindrance can impose an attack to occur on the pole having the same sign as the ion. That is what probably happens in the case of water/MeOH mixtures where water molecules could have made many interactions with the methylene group due to their very high dissociating power (very high dielectric constant, Table 1). In this case, the methylene group would be very solvated by water, and there would be then no more dipoles on the positive side available for OH$^-$ attack. That could explain the negative slope exhibited by the plots in Figure 3 and the relative high-calculated value for *r* in the case of condensations run in water/MeOH mixtures.

These results could also partially explain the different apparent orders found in the literature,[6−11] the modifications mentioned being probably due to the nature and the purity of the solvents employed. Finally, in our experimental conditions, results show clearly that the reaction rate and then the yield as a function of reaction

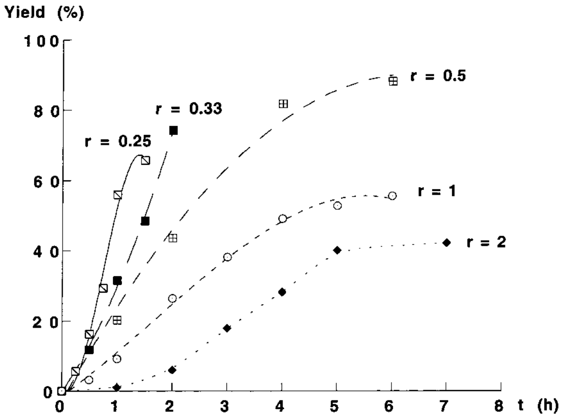


Figure 4. Knoevenagel condensation of **2** and **4** in nonstoichiometric conditions in pure methanol. $[\mathrm{Base}]_0/[\mathrm{CH_2CN}]_0 = 50\%$ and $[\mathrm{CH_2CN}]_0 = 0.06$ mol $\mathrm{L^{-1}}$. $r = [\mathrm{CH_2CN}]_0/[\mathrm{CHO}]_0$ and $T = 65$ °C.

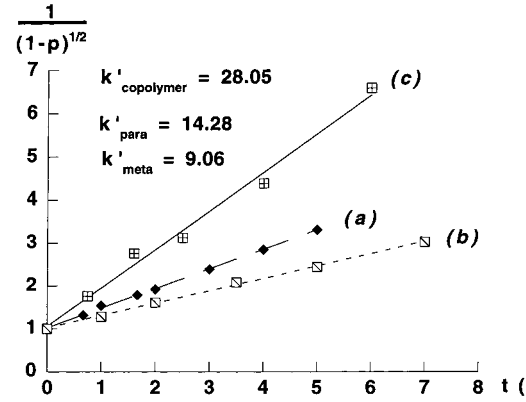


Figure 5. Knoevenagel condensation in stoichiometric conditions in THF/methanol mixtures ($^2/_3$, $^1/_3$ volume) with $[\mathrm{base}]_0/[\mathrm{CH_2CN}]_0 = 50\%$ and $[\mathrm{CH_2CN}]_0 = 0.06$ mol $\mathrm{L^{-1}}$ at 65 °C. The apparent order is equal to 1.5 as well in the case of the two model reactions between **4** and **2** (a) or **6** (b) as in the case of the copolymerization between **1** and **6** (c). Apparent rate constants are given in $\mathrm{L^{1/2}\ mol^{-1/2}\ h^{-1}}$, and p is the acetonitrile function conversion calculated from the quantity of polymer recovered.

time can be shrewdly adjusted by the control of the dielectric constant of the initial medium. More importantly, it will permit the control of the molecular weight and then the solubility of polymers as far as polymerization occurs via the Knoevenagel condensation, the insolubility of polymers being essentially attributed to the rigidity of macromolecular chains.[21]

2. Nonstoichiometric Conditions. To verify the zero order with respect to the aldehyde, kinetics of the Knoevenagel condensation of **2** and **4** was examined in methanol at 65 °C with an excess of aldehyde functions with regard to the acetonitrile concentration functions. The results obtained are reported in Figure 4. Surprisingly, the apparent order decreases with decreasing the stoichiometric ratio r ($r = [\mathrm{CH_2CN}]_0/[\mathrm{CHO}]_0$). This is in contrast with the zero order with aldehyde determined previously since there is an effect of the aldehyde concentration on the kinetics. This behavior has already been observed by Boileau[5] and Patai et al.,[6] namely, a zero order in aldehyde although the aldehyde has some influence on the overall rate of the reaction. Considering the previous conclusion about the solvent effect and the fact that the aldehyde compound is a polar molecule, we can imagine the formation of a complex between the aldehyde and the methylene compound. Such aggregated species may be held together by interaction between the $-\mathrm{C{=}O}$ dipole of the aldehyde and the $-\mathrm{C{-}H}$ dipole of the active methylene compound. Therefore, the more aldehyde molecules in the medium, the more the methylene group is "solvated" by the aldehyde. That may explain the decrease of the apparent order of the reaction with the increase of the aldehyde excess. Moreover, as the presence of dissociating species like aldehyde facilitates the reaction between the methylene group and $\mathrm{OH^-}$, the increase of the reaction rate is then attributed to the complex formation.

Kinetic Study of the Knoevenagel Condensation in THF/MeOH Mixtures. As the copolymerization of **1** and **2** (Scheme 2) is impossible in pure methanol because the monomer **1** and the forming polymer **3** are insoluble in alcohols, it is then necessary to use both an alcohol to make soluble the base and THF to dissolve **1** and **3**. Thus, the kinetics of the model reaction between **2** and **4** (Scheme 3) must also be examined in refluxing THF/MeOH mixtures (65–66 °C).

Many experiments have shown that the best compromise between the solubility of **5** and the reaction rate has been found for a solvent mixture composed with $^2/_3$ of THF and $^1/_3$ of MeOH in volume. However, in these experimental conditions, we observed a modification of the apparent order, which is equal to 1.5 instead of 1. This can be explained by the fact that the overall order and the molecularity of the rate-determining step would be a result of the relative rate ratios steps 1 and 2. Effectively, the third step being very fast,[28] it seems unlikely that the nonprotonic solvent (THF) force the alcohol anion in step 3 to consume a proton in the activated methylene group instead of the protonized base. Moreover, the intermediate in step 3 should not be able to attack the methylene group because of its steric bulkiness and the presence of the cyano group in its vicinity, which has a contrary attractive inductive effect. Thus, the apparent order equal to 1.5 would be due to the relative rate ratio between steps 1 and 2. In this hypothesis,

$$-\frac{\mathrm{d}[\mathrm{CH_2CN}]}{\mathrm{d}t} = k'[\mathrm{CH_2CN}]^{3/2} \tag{3}$$

After integration,

$$\frac{1}{[\mathrm{CH_2CN}]^{1/2}} = \frac{1}{[\mathrm{CH_2CN}]_0^{\ 1/2}} + k't \tag{4}$$

or

$$\frac{1}{(1-p)^{1/2}} = 1 + [\mathrm{CH_2CN}]_0^{\ 1/2}k't \tag{5}$$

with p the conversion in acetonitrile functions. The apparent rate constant k'_{para} of the model reaction described in Scheme 3 was found to be equal to 14.28 $\mathrm{L^{1/2}\ mol^{-1/2}\ h^{-1}}$ (Figure 5a).

Unfortunately, the poly[bicarbazolylene-*alt*-*p*-phenylenebis(cyanovinylene)] (**3**) becomes rapidly insoluble in this reactional medium. We have chosen then to study the polycondensation of the *m*-phenylenediacetonitrile (**6**) instead of *p*-phenylenediacetonitrile (**2**) as the active methylene compound. Before starting the study of the polycondensation, we have examined the kinetics of the condensation of **4** and **6** in refluxing THF/MeOH mixtures ($^2/_3$ of THF and $^1/_3$ of MeOH in volume). The

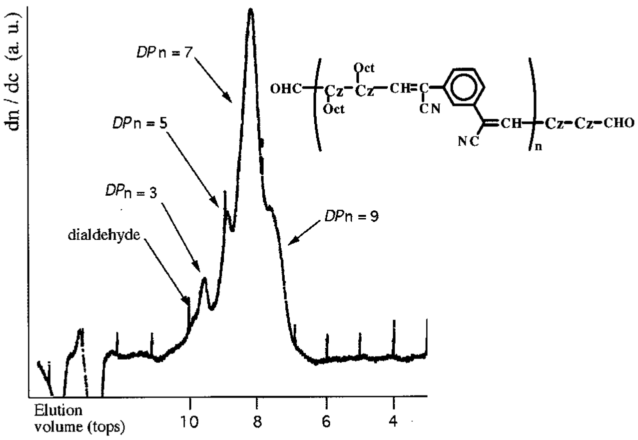


Figure 6. Size exclusion chromatogram of poly[bicarbazolylene-*alt*-*m*-phenylenebis(cyanovinylene)] obtained after a polymerization time equal to 1.6 h. The scheme above represents the general molecular formula of the oligomers with $\mathrm{DP_n} = 2n + 1$. $\overline{\mathrm{DP}}_{\mathrm{n,SEC}}$ of the mixture of oligomers is estimated from the relative proportion of each peak: $\overline{\mathrm{DP}}_{\mathrm{n,SEC}} = 0.056 \times 1 + 0.104 \times 3 + 0.193 \times 5 + 0.451 \times 7 + 0.197 \times 9 = 6.3$.

apparent order of this second model reaction at 65 °C is also equal to 1.5, and $k'_{\mathrm{meta}} = 9.06\ \mathrm{L^{1/2}\ mol^{-1/2}\ h^{-1}}$ (Figure 5b). As expected, the *m*-phenylenediacetonitrile is less reactive than **2** because of the attractive inductive effects which are less important in meta position than in the para.

Copolymerization via the Knoevenagel Condensation. The polycondensation of **1** and *m*-phenylenediacetonitrile (**6**) occurred in THF/MeOH mixtures ($^2/_3$, $^1/_3$ in volume) at 65 °C with tetrabutylammonium hydroxide as catalyzer. From the quantity of poly[bicarbazolylene-*alt*-*m*-phenylenebis(cyanovinylene)] (**7**) obtained, it is possible to estimate *p*, the acetonitrile function conversion, and an apparent order equal to 1.5 was found. Thus, the bicarbazyldialdehyde **1** in place of the carbazylmonoaldehyde **4** does not modify the reaction mechanism. However, the rate of the polycondensation is higher than that of the corresponding model reaction at the same temperature since the apparent constant is equal to $28.05\ \mathrm{L^{1/2}\ mol^{-1/2}\ h^{-1}}$ instead of $9.06\ \mathrm{L^{1/2}\ mol^{-1/2}\ h^{-1}}$ (Figure 5). This result can be explained by the increase of the interactions between the methylene compound and the dialdehyde probably due to the higher local dipole in dialdehyde **1** with regard to monoaldehyde **4**. The approach of $\mathrm{OH^-}$ would be facilitated, and then the reaction rate accelerated.

The copolymers were analyzed by steric exclusion chromatography (SEC). The molecular weight of the copolymer obtained after 8 h is equal to 7500 g mol^{-1} (in polystyrene equivalent). A wholly THF-soluble copolymer obtained in 48 h has displayed $\overline{M}_{\mathrm{n}} = 25\,000$ ($\overline{DP}$)=67. For polycondensations occurring in less than 5 h, we have obtained oligomers, and the chromatograms are polymodal (Figure 6): each peak corresponds to one size of oligomer. Effectively, macromolecules being exclusively finished by aldehyde functions,[21] chromatograms display the remaining monomer and macromolecules of $\mathrm{DP_n} = 3$, 5, 7, and 9 (Figure 6). The relative proportion of oligomers changes with polycondensation time as expected in polycondensation. At $t = 2.5$ h ($p = 0.898$), there is practically no more dialdehyde remaining, and the oligomer of $\mathrm{DP_n} = 9$ appears only from $t = 1.6$ h ($p = 0.869$). In the case of oligomers, we observed a very good correlation between the $\overline{\mathrm{DP}}_{\mathrm{n}}$ calculated by FTIR[21] and those obtained by SEC analyses. (For high molecular weight, chain ends are not observable by FTIR and $\overline{\mathrm{DP}}_{\mathrm{n,FTIR}}$ cannot be calculated.) However, there is a big differences in the calculated values of $\overline{\mathrm{DP}}_{\mathrm{n}}$ and the theoretical $\overline{\mathrm{DP}}_{\mathrm{n,th}}$ ones ($\overline{\mathrm{DP}}_{\mathrm{n,th}} = 1/(1 - p)$) (Table 2). This is probably due to the nonisoreactivity of the two acetonitrile functions since all macromolecules have exclusively CHO extremities, the second Knoevenagel condensation on the second acetonitrile function of the active methylene monomer being faster than the first one. Moreover, even if the reaction medium seems homogeneous, we cannot exclude the precipitation of any oligomers in the medium that could limit the polycondensation reaction.

Table 2. Polycondensation of 1 and 6 in Refluxing THF/MeOH Mixtures ($^2/_3$, $^1/_3$ Volume); Comparison of Values of Theoretical $\overline{\mathrm{DP}}_{\mathrm{n,th}}$ and Calculated $\overline{\mathrm{DP}}_{\mathrm{n}}$ from FTIR[21] and SEC Measurements[a] as a Function of Time or *p*, the Monomer Conversion

t (h)	p^b	$\overline{\mathrm{DP}}_{\mathrm{n,th}} = 1/(1 - p)$	$\overline{\mathrm{DP}}_{\mathrm{n,SEC}}$	$\overline{\mathrm{DP}}_{\mathrm{n,FTIR}}$
0.75	0.676	3.1	5.1	3.7
1.6	0.869	7.6	6.3	5.4
2.5	0.898	9.8	7.1	6.4
4	0.948	19.2	7.4	7.5
6	0.977	43.5	11.5[c]	9.3
8	0.995	200	20.3[c]	16.1

[a] Assuming two aldehyde end groups per chain.[21] Each peak corresponds to one type of oligomer (see Figure 6). [b] *p* calculated from the polymer quantity recovered. [c] $\overline{\mathrm{DP}}_{\mathrm{n}}$ estimated in polystyrene equivalent.

Experimental Section

Tetrahydrofuran (THF), 2-propanol (iPrOH), *tert*-butyl alcohol (tBuOH), and methanol (MeOH) were distillated prior to utilization. Tetrabutylammonium hydroxide in solution in methanol (1 M), *p*- and *m*-phenylenediacetonitrile, and *N*-ethylcarbazolecarboxaldehyde (ACROS Organics and Aldrich) were used as received. Synthesis of the dialdehyde **1** was previously described.[21] All reactions were performed under nitrogen. Syntheses of polymers and model compounds are shown in Schemes 2 and 3. Example of the condensation between **4** and **6** in a THF/MeOH mixture with $[\mathrm{base}]_0/[\mathrm{CH_2CN}]_0 = 50\%$: in a 100 mL three-necked flask fitted with a reflux condenser, 500 mg (2.24 mmol) of **4** and 175 mg (2.24 mmol) of **2** were dissolved in 23.3 mL of THF and 11.7 mL of MeOH. A 1.12 mL aliquot of $\mathrm{Bu_4NOH}$ in methanol (1 M) is added at reflux (65−66 °C). After refluxing for the suitable time, reaction was stopped by adding of 30 mL of MeOH in order to favor the precipitation of product and cooling the reaction medium at 0 °C for 5 min. The resulting solid obtained was then filtered off and purified by Soxhlet extraction with methanol. Yellow powders were obtained in good yields. ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, ppm): $\delta = 1.4$ (t; $\mathrm{CH_3}$), 4.3 (q; $\mathrm{CH_2}$), 7.3−7.66 (m; carbazole), 7.74−8.1 (m; phenyl and carbazole), 8.6 (s; $\mathrm{H^4}$). ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, ppm): $\delta = 13.8$ ($\mathrm{CH_3}$), 37.7 ($\mathrm{CH_2}$), 106.2 ($\mathrm{C^{11}}$), 108.8 ($\mathrm{C^8}$), 109.9 ($\mathrm{C^1}$), 119.0 ($\mathrm{C^{12}}$), 119.8 ($\mathrm{C^4}$), 120.6 ($\mathrm{C^7}$), 122.5 ($\mathrm{C^{5,6}}$), 123.0 ($\mathrm{C^{16}}$), 124.3 ($\mathrm{C^3}$), 125.6 ($\mathrm{C^{15}}$), 126.5 ($\mathrm{C^{2,14,18}}$), 127.1 ($\mathrm{C^{4b}}$), 129.6 ($\mathrm{C^{4a}}$), 135.6 ($\mathrm{C^{13}}$), 140.3 ($\mathrm{C^{8a}}$), 141.0 ($\mathrm{C^{10}}$), 144.3 ($\mathrm{C^{9a}}$). Characterizations of **1**, **3**, and **5** have already been given.[21,22] The ^{1}H NMR spectrum of the mustard-colored copolymer **7** is similar to the copolymer **3** spectrum already published.[21] FTIR spectra were recorded on a Perkin-Elmer 1600. SEC measurements were performed in THF with Ultrastyragel or Microstyragel columns (100, 500, 10^3, 10^4, and 10^5 Å) equipped with a differential refractometer (Waters). Polystyrene standards (Aldrich) were used for calibration.

Conclusions

We have shown that the Knoevenagel condensation was effective with *N*-ethylcarbazolecarboxaldehyde and *p*- or *m*-phenylenediacetonitrile with tetrabutylammonium hydroxide as catalyzer. In methanol, the reaction is of order 1, and the step of the formation of the partially ionized intermediate determines the reaction rate. In THF/methanol mixtures, the rate-determining step is a result of the relative ratio rate steps 1 and 2.

We have shown that the different apparent orders mentioned in the literature could be partially explained by the effect of the dissociating power and the purity of solvents used. The reaction rate and then the yield as a function of reaction time could be precisely controlled by the choice of the dielectric constant of the initial medium.

According to these results, we have successfully polycondensated the *N*,*N*′-dioctylbicarbazyl-3,3′-dicarboxaldehyde with the *m*-phenylenediacetonitrile in THF/methanol mixtures. The polycondensation occurs in homogeneous media and obeys the same reaction mechanism as that determined for the model reaction led in the same experimental conditions. However, the polycondensation is more than 3 times faster than the model reaction. The presence of dialdehyde in the place of monoaldehyde increases the reaction rate because of the higher polar interactions between the dialdehyde and the methylene active group that are supposed to assist the dissociation of the methylene compound.

Wholly THF-soluble polymers obtained can reach molecular weight equal to 25 000, in polystyrene equivalent. They exhibit remarkable photo- and electroluminescent properties, which will be presented in a forthcoming paper.

References and Notes

(1) Knoevenagel, E. *Ber.* **1894**, *27*, 2346.
(2) (a) Knoevenagel, E. *Ber.* **1898**, *31*, 738. (b) Knoevenagel, E. *Ber.* **1898**, *31*, 2596.
(3) Hann, G.; Lapworth, A. *J. Chem. Soc.* **1904**, *85*, 46.
(4) Cope, A. C. *J. Am. Chem. Soc.* **1937**, *59*, 2327.
(5) Boileau, *J. Bull. Soc. Chim. Fr.* **1954**, 758.
(6) Patai, S.; Israeli, Y. *J. Chem. Soc.* **1960**, 2020.
(7) Rodriguez, I.; Sastre, G.; Corma, A.; Iborra, S. *J. Catal.* **1999**, *183*, 14.
(8) Patai, S.; Edlitz-Pfeffermann, J.; Rozner, Z. *J. Am. Chem. Soc.* **1954**, *76*, 3446.
(9) Patai, S.; Israeli, Y. *J. Chem. Soc.* **1960**, 2025.
(10) Patai, S.; Zabicky, J. *J. Chem. Soc.* **1960**, 2030.
(11) Patai, S.; Israeli, Y. *J. Chem. Soc.* **1960**, 2038.
(12) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179.
(13) Best, J.; Thorpe, J. F. *J. Chem. Soc.* **1909**, *95*, 685.
(14) Ziegler, K.; Eberle, H.; Ohlinger, H. *Ann.* **1933**, *504*, 94.
(15) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
(16) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friends, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(17) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.
(18) Romero, D. B.; Schaer, M.; Leclerc, M.; Ades, D.; Siove, A.; Zuppiroli, L. *Synth. Met.* **1996**, *80*, 271.
(19) Romero, D. B.; Nüesch, F.; Benazzi, T.; Ades, D.; Siove, A.; Zuppiroli, L. *Adv. Mater.* **1997**, *9*, 1158.
(20) Bacsa, W. S.; Schaer, M.; Zuppiroli, L.; Ades, D.; Siove, A. *J. Appl. Phys.* **1998**, *84*, 5733.
(21) Boucard, V.; Benazzi, T.; Adès, D.; Sauvet, G.; Siove, A. *Polymer* **1997**, *38*, 3697.
(22) Boucard, V.; Adès, D.; Siove, A.; Romero, D.; Schaer, M.; Zuppiroli, L. *Macromolecules* **1999**, *32*, 4729.
(23) Knoevenagel, E. *Ber.* **1896**, *29*, 172.
(24) Cope, A. C.; Hoffmann, C. M.; Wyckoff, C.; Hardenbergh, E. *J. Am. Chem. Soc.* **1941**, *63*, 3452.
(25) Heitler, C. *J. Chem. Soc.* **1963**, 4885.
(26) Born, M. *Z. Phys.* **1920**, *1*, 45.
(27) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 51.
(28) Reeves, R. L.; Patai, S. In *The Chemistry of Carbonyl Group*; Interscience: New York, 1966; p 567.

MA002233G