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Step-Growth Polymerization of Terephthaldehyde Catalyzed by *N*-Heterocyclic Carbenes

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Introduction. Benzoin condensation is a C−C bond forming reaction by self-condensation of benzaldehyde, leading to an aromatic β-keto alcohol called benzoin. This reaction is generally catalyzed by azolium salts (thiazolium, imidazolium, and triazolium) in the presence of a strong base. This topic has been the matter of intensive research,[1,2] focused in particular on the design of asymmetric catalysts that could generate optically active benzoin since such a condensation creates a stereogenic center. The mechanism of this reaction was first unveiled in 1958 by Breslow et al.,[3] who demonstrated that the catalytic species is a carbene which is formed in situ by deprotonation of the azolium salt by a strong base; this carbene acts as a nucleophilic catalyst that activates the carbonyl of benzaldehyde, forming a resonance-stabilized enaminol-type "Breslow intermediate". Subsequent condensation with a second benzaldehyde molecule regenerates the carbene catalyst. On the basis of this general study, numerous organocatalytic systems—asymmetric or not—including NHCs (*N*-heterocyclic carbenes) have been developed to this end. Crossed intermolecular aldehyde−ketone or intramolecular aldehyde−aldehyde condensations aiming the synthesis of biologically active cyclic hydroxyketones have also been reported, though more recently.[4] Surprisingly, reports describing the condensation of bis-aldehyde molecules such as terephthaldehyde and targeting the formation of a polymer by step-growth polymerization are very scarce. Indeed, only two attempts at synthesizing the corresponding polymers from bis-aldehydes could be found, and it was resorted in both cases to cyanides as catalysts,[5,6] the poly(1,4-phenylene-1-oxo-2-hydroxyethylene) formed, also referred to as polybenzoin, serving as precursors for poly(1,4-phenylenevinylene) (PPV) derivatives and high-performance polyquinoxalines, respectively.

In the past decade, NHCs have been featured as highly efficient organic catalysts for miscellaneous reactions of molecular chemistry.[1−4,7−11] Their potential in organo-catalyzed polymerizations has also been exploited by Hedrick, Waymouth et al.,[12−14] and our group as well.[15,16] Noteworthy, most of NHC-triggered polymerizations investigated so far are chain growth polymerizations, including the group transfer polymerization (GTP) of (meth) acrylic monomers[14,15] and the ring-opening polymerization (ROP) of cyclic siloxanes,[17] cyclic esters,[12,13] and ethylene oxide.[16] In contrast, the use of NHCs as organocatalysts for step-growth polymerization has not attracted the same interest, the report by Hedrick et al. describing the NHC-catalyzed synthesis of poly(ethylene terephtalate) being the sole found in the literature.[18] In this investigation we aim at using NHCs instead of potentially toxic cyanide ions as catalysts for the step-growth polymerization of terephthaldehyde. We show that polybenzoins can be obtained in the presence of NHCs under mild conditions. The effect of parameters such as the type of NHC, the reaction time, and the type of solvent on molecular features of the polybenzoin formed, such as the presence of macrocyclics, is discussed.

Experimental Section. *Materials.* All the experiments were performed under an inert atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents and monomers were employed. THF was distilled over Na/benzophenone prior to use. DMSO was refluxed over CaH_2 and was distilled under vacuum prior to use. Terephtaldehyde was purchased from Alfa Aesar and was dried azotropically with dioxane. *N*-Heterocyclic carbenes NHC-3 and NHC-4 were purchased from Sigma and STREM chemicals and were used as such without further purification.

Synthesis of NHCs. NHC-1 and NHC-2 were prepared by slightly modifying already reported procedures.[15,19] Diisopropylimidazolium salt was deprotonated with NaH and a catalytic amount of *t*-BuOK, where as ditetrabutylimidazolium salt was deprotonated with *n*-BuLi. NHC-1 was purified by distillation under reduced pressure where as NHC-2 was purified by sublimation.

Instrumentation. ^{1}H NMR spectra were recorded on Bruker AC-400 spectrometer in appropriate deuterated solvents.

Molar masses were determined by gel permeation chromatography (GPC) using a PL-GPC50 plus Integrated GPC System equipped with TSK columns (G2000, G3000, and G4000HXL with pour sizes of 20, 75, and 200 Å, respectively, connected in series) fitted with both refractometric and UV detectors and THF as the mobile phase at a flow rate of 1 mL/min. Trichlorobenzene was used as a flow marker. The molar masses of polybenzoin were determined as follows (see also Supporting Information). In the low molar mass region, GPC revealed a series of discrete peaks which were attributed to the different *n*-mers (dimer, trimer, tetramer, etc., up to the heptamer) of linear polybenzoin, since no cyclic polymer was detected in the early stages of the polymerization. The ratio, noted $M_{PS}/M_{polybenzoin}$, between the apparent molar mass (M_{PS}) based on a linear calibration using polystyrene standards and the molar mass of the linear polybenzoin ($M_{polybenzoin}$) of the *n*-mers was found to increase linearly with $M_{polybenzoin}$ from the dimer to the heptamer (Figure S2). This linear variation was extrapolated to higher molar masses to elaborate a "virtual" calibration curve based on linear polybenzoins (Figure S3).

Differential scanning calorimetry (DSC) measurements were performed on a DSC Q100 apparatus from TA Instruments. Data were recorded during the second run for temperatures ranging from 20 to 200 °C at a heating rate of 10 °C min^{-1}. The cooling rate between the first and second runs was also equal to 10 °C min^{-1}. The glass transition temperature (T_g) was given by the inflection point of the transition.

Polymerizations. All polymerization reactions were carried out under a dry and inert atmosphere using vacuumed flame-dried special Schlenk apparatus equipped with

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Table 1. Step-Growth Polymerization of Terephthaladehyde in the Presence of NHC[a]

run	NHC	solvent	% NHC	run time (h)	conv[b] (%)	M_n (PDI)[c]	M_w[c]	$M_{n(NMR)}$	% cyclics
1	1	THF	1	24	2.5	365 (1.30)	480	nd	nd
2	2	THF	1	24	3.0	420 (1.39)	585	nd	nd
3	3	THF	1	24	4.4	425 (1.47)	625	nd	nd
4	4	THF	1	3	81.3	690 (1.40)	970	720	3.7
5	4	THF	1	17	91.0	750 (1.41)	1060	1495	49
6	4	THF	1	24	91.4	765 (1.41)	1075	1555	51
7	4	THF	1	72	92.2	850 (1.54)	1150	1720	
8	4	THF	1	170	93.3	820 (1.32)	1086	1975	
9	4	DMSO	1	24	78.3	650 (1.43)	930	620	0
10	4	DMSO	1	72	82	705 (1.36)	955	745	5
11	4	DMSO	1	170	85.6	650 (1.52)	990	925	30
12	4	THF	0.5	24	83.5	670 (1.45)	970	815	20
13	4	THF	5	24	93.3	nd	nd	3120	nd
14	4	THF + DMSO	1	24	81.5	680 (1.38)	940	725	6
15	4	THF + DMSO	1	72	86.9	875 (1.46)	1275	1020	15
16	4	THF + DMSO	1	170	91.2	880 (1.45)	1270	1520	42

[a] Conditions: 1 g of terephthaldehyde, 10 mL of solvent; reaction temperature is 40 °C; nd = not determined. [b] Conversions of the monomer were calculated by end-group analysis using ^{1}H NMR. [c] M_n, M_w, and PDI were determined by GPC in THF as eluent.

a withdrawal vial on the side of the main flask. In a typical procedure, a 50 mL flame-dried special Schlenk apparatus was charged with 1 g of terephthaldehyde (7.45 mmol), 22 mg of NHC-4 (0.074×10^{-3} mol), and 10 mL of THF (or DMSO). The Schlenk tube was left under stirring in an oil bath at 40 °C. At precise time intervals, aliquots were withdrawn through vacuum flame-dried withdrawal vial attached to the flask. A droplet of degassed MeOH was then introduced, and the aliquot was removed from the withdrawal vial. At the end, the reaction was quenched by adding few drops of methanol to the reaction mixture. The polybenzoin was precipitated in water and dried under vacuum. Molecular characteristics of polybenzoins are provided in Table 1.

Determination of the Content of Cyclics. The number of cyclics, C, is determined as follows:

$$C = T - N_0(1-p)$$

where T is the total number of molecules, including cyclics and linear polymers.

Since $M_n = M_0 N_0 / T$, therefore C/T, the fraction of cyclics, is

$$C/T = 1 - (M_n/M_0)(1-p)$$

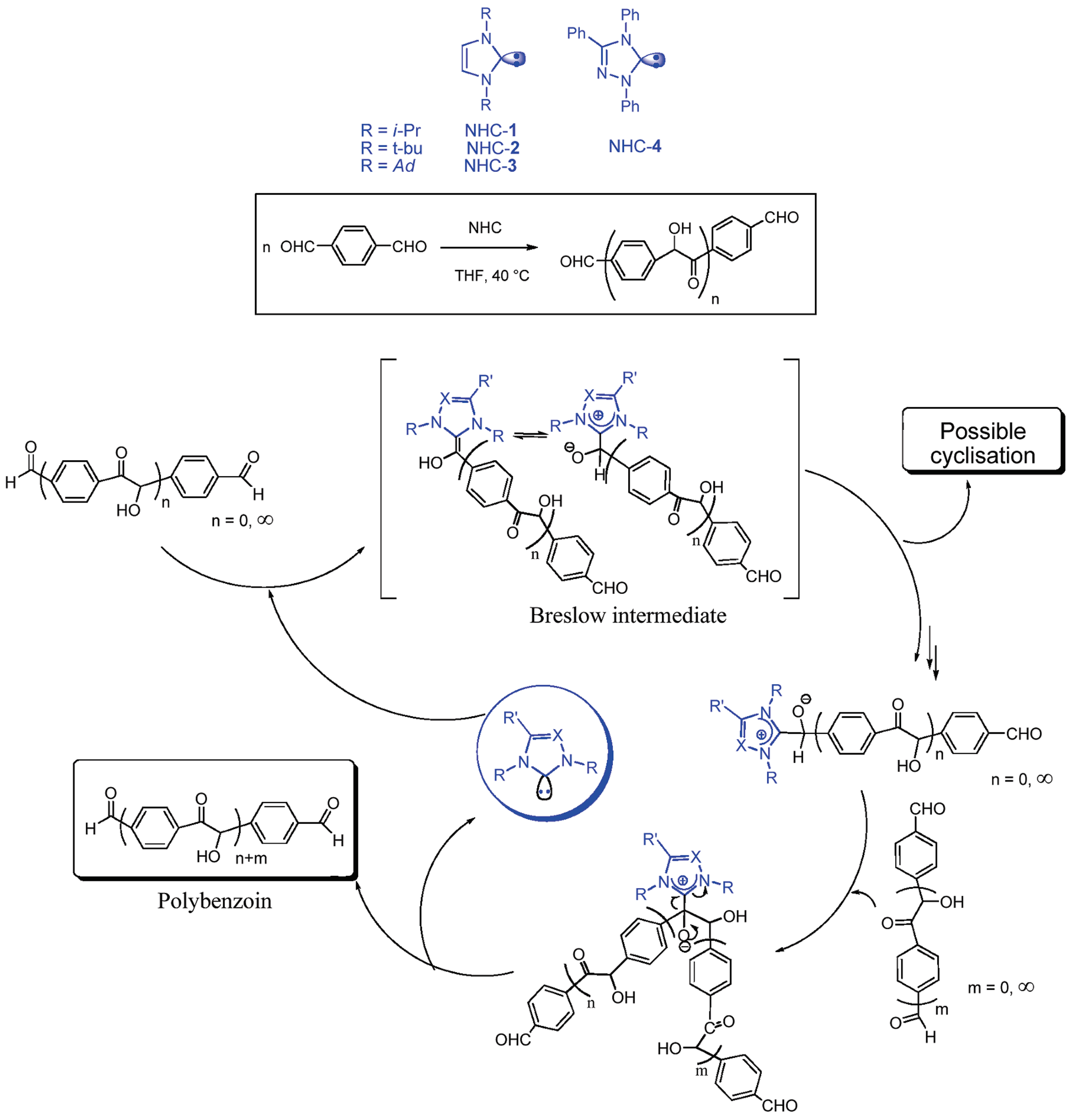
where p stands for the monomer conversion obtained by ^{1}H NMR spectroscopy, M_n stands for the number-average molar mass of the polymers determined by GPC, and M_0 is the molar mass of the 1,4-phenylene-1-oxo-2-hydroxyethylene monomer unit.

Results and Discussion. Four different *N*-heterocyclic carbenes (NHCs) were employed to catalyze the step-growth polymerizations of terephtaldehyde carried out, in first instance, in solution at room temperature (Scheme 1). NHC-3 and -4 are commercially available (Aldrich), while NHC-1 and -2 can be obtained with a high chemical purity, by slightly modifying already published procedures.[15,19] The conversion and molar masses of the polybenzoin samples thus obtained were greatly influenced by the type of carbene employed. Out of the four catalysts, NHC-4 afforded the highest conversions along with the highest molar masses, their respective efficiency corresponding to the following order (Figure 1a): NHC-1 ≈ NHC-2 < NHC-3 ≪ NHC-4 (Table 1). It is difficult to correlate the activity of these NHCs to their nucleophilicity and/or to their pK_a values, though NHC-1 and NHC-2 have almost the same pK_a.[20] The higher reactivity of the triazolylidene carbene (NHC-4) compared to the imidazolylidene NHCs (NHC-1 to NHC-3) might reflect a faster kinetic of proton exchange of the corresponding azolium salts, as discussed previously by Enders et al.[20a]

A minimum of 1 mol % of NHC relative to terephthaladehyde was required to observe the formation of a polymer. Further increase of the content in NHC, from 1 to 5 mol %, did not significantly increase the rate of polymerization (Table 1, runs 6 and 13). The polymers could be purified by precipitation in water to eliminate the nonreacted monomer. One can clearly observe the presence of dimer, trimer, and other *n*-mers on the GPC traces. We found that a temperature of 40 °C was appropriate to achieve reasonable yields (> 93%); below this temperature, the reaction was sluggish, and higher temperatures were not tried in this first set of experiments. The step-growth polymerization of terephthaldehyde carried out in the presence of NHC-4 was further investigated. Aliquots were taken at different time intervals to monitor the polymerization kinetics. The molar mass of polybenzoin increased with time (Table 1), as expected in a step-growth polymerization,[21] but no significant increase of the percent monomer conversion was observed beyond 24 h up to 72 h. ^{1}H NMR spectroscopy was used to determine the monomer conversion that was deduced upon comparison of the peak intensities of the aldehyde protons carried by the nonreacted monomer and the polymer chain ends to those of the aromatic protons. A representative ^{1}H NMR spectrum of polybenzoin recorded in DMSO-d_6 is shown in Figure 2. The relative complexity of the signals due to the protons of benzylic and hydroxyl groups seen between 6 and 6.5 ppm is attributable to the formation of stereogenic centers of the 1,4-phenylene-1-oxo-2-hydroxyethylene monomer units, which in turn gave rise to different enantiomorphs. From the literature available on benzoin condensation, it is highly likely that the step-growth process of bis-aldehydes described here occurs by the same mechanism, involving the formation of an enaminol-type Breslow intermediate at each step, as highlighted in Scheme 1.

After 72 h of reaction in THF at 40 °C, the polybenzoin formed tends to precipitate out of the solution, which is mirrored in the plateau reached by the monomer conversion. The GPC traces of the fraction soluble in THF did not show the formation of new set of oligomers, meaning that the vast majority of the monomer was consumed within 72 h. When characterized by GPC using THF as eluent (Figure 1b), the polymer formed after a prolonged reaction period of 1 week

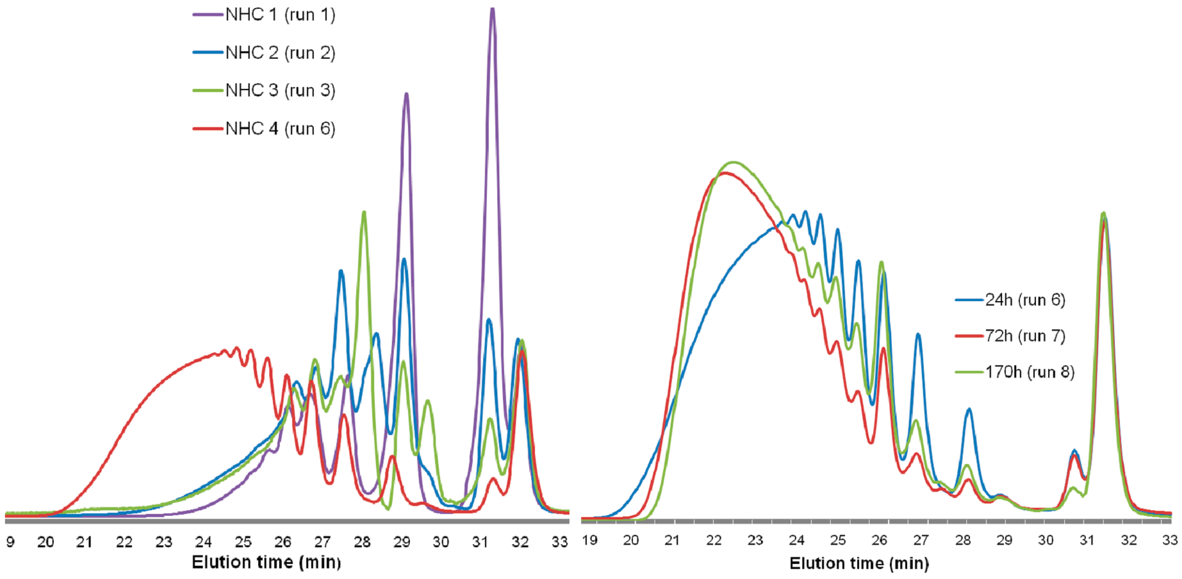
Scheme 1. Different *N*-Heterocyclic Carbenes Employed in This Study and Proposed Catalytic Pathway Showing the Breslow Intermediate during NHC-Catalyzed Step-Growth Polymerization of Terephthaldehyde



exhibited a lower M_n than that of the previous aliquots owing to the precipitation of longer polybenzoins in this solvent. DMSO being a better solvent of polybenzoin compared to THF, analysis by ^{1}H NMR spectroscopy in DMSO-d_6 of the whole reaction mixture (precipitated + soluble fractions formed in THF) showed an increase of the molar mass (M_n), compared to the former aliquot. M_n values drawn from ^{1}H NMR analysis in DMSO-d_6 were thus calculated assuming a truly linear step-growth process, assuming that no cyclics were formed as side products. As a matter of fact, the mismatch between M_n values obtained by ^{1}H NMR spectroscopy and by GPC is an indication of the presence of cyclic polybenzoins. In the Experimental Section is explained how the fraction of cyclics can be calculated. In contrast to what is expected from regular step-growth polymerizations, the formation of cyclics is not favored in the initial phase of the reaction, likely due to the rigidity and the persistence length of the polybenzoin generated. However, in the later phase of polymerization that is at higher conversion, the extent of cyclics tends to increase, suggesting that this system generate cyclics of much bigger size than would do flexible polymers. The solvent seems to play a role as well in the extent of cyclics formed: the poorer the quality of the solvent is, the higher the extent of cyclics is (Table 1, entries 6, 9, and 14).

The isolated polybenzoins were also characterized by DSC which did not indicate any melting point, all compounds being amorphous in nature with a glass transition temperature (T_g) value increasing with the molar mass. For instance, the T_g measured for polymers of molar mass (by ^{1}H NMR) 1035, 1340, and 1670 g·mol^{-1} are 112, 137, and 149 °C, respectively.

In an attempt to avoid the precipitation of polymers of large size formed at high conversion, DMSO was substituted for THF, the former being a better solvent for polybenzoin. In the latter case, the reaction kinetic was slower and molar masses of polybenzoins obtained in DMSO were found lower compared to those of samples synthesized in THF under similar reaction conditions (Table 1). Next, a mixture of THF and DMSO was used



(a) **(b)**

Figure 1. GPC overlay of polybenzoins (a) obtained from the four different NHC catalysts and (b) obtained with NHC-4 at different time intervals.

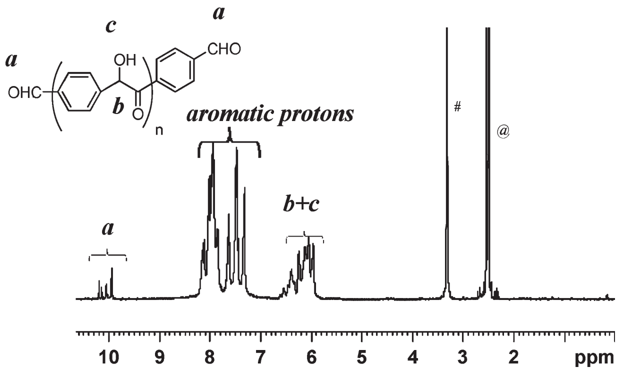


Figure 2. ^{1}H NMR spectrum in DMSO-d_6 of polybenzoin obtained with NHC-4 (Table 1, run 9) after precipitation in water (@, # correspond to solvent residual peaks).

as solvent in an attempt to retain both a fast reaction and the solubility of polybenzoin. However, the results obtained in terms of conversion and molar masses appear to be intermediate between those generated in THF and DMSO. As a matter of fact, the faster path of reaction in THF, which is not a good solvent for the polymer formed, is indicative of the existence of conditions that favor the association of these aromatic molecules likely by $\pi-\pi$ stacking interactions, be it the monomer, dimer, etc. The reaction becomes sluggish only when polybenzoins of larger size are produced and tend to precipitate. In DMSO, which is a good solvent, any such association between molecules would be disrupted, the latter being totally soluble in such a dissociating medium; it results in a slower path of reaction.

In summary, *N*-heterocyclic carbenes (NHCs) proved efficient organocatalysts for step-growth polymerization of terephthaldehyde in solution at 40 °C, leading to amorphous poly(l,4-phenylene-l-oxo-2-hydroxyethylene) referred to as polybenzoin. This work confirms that NHCs should be preferred to cyanide ions used so far, which can release cyanohydric acid in the presence of water. Work is currently progressing under different experimental conditions (higher temperature, lower concentration) in order to minimize the extent of cyclics formed at higher conversion. The use of optically active auxiliaries to induce asymmetric step-growth polymerization of bis-aldehydes is also in progress.

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Supporting Information Available: Discussion of how GPC calibration for polybenzoins was realized. This material is available free of charge via the Internet at http://pubs.acs.org.

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