

Synthesis and Dielectric Properties of Hyperbranched CuPc Based on Biphenyl Segments

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Three hyperbranched copper phthalocyanine (HBCuPc) oligomers based on biphenyl segments have been successfully synthesized. Rigid rod semiconductor material with good solubility, small dispersion of the dielectric constant, and low dielectric loss was obtained by solution suspension. The content of the CuPc unit in HBCuPc was increased by increasing the prepolymerization time from 12 h to 36 h. The dielectric loss was slightly influenced by temperature but remained stable below 100°C. Furthermore, the obtained novel HBCuPc materials have potential for applications as organic dielectric materials.

Key words: Hyperbranched copper phthalocyanine, dielectric properties, biphenyl segments, CuPc, HBCuPc

INTRODUCTION

In recent years, organic semiconductors have attracted considerable interest due to their growing potential as active materials for use in high-energy and pulsed capacitors.¹ In particular, materials which demonstrate desired dielectric properties at high operating frequency (>1 kHz) are actively sought.^{2–7} Copper phthalocyanine (CuPc) materials, with good dielectric responses due to the space-charge effect, have been employed as excellent capacitors in industrial applications.^{8–10} However, the dielectric loss of these percolative systems is generally large.^{11–14} On the other hand, hyperbranched polymers have attracted more attention from polymer scientists, because of their unique structural characteristics, synthetic methods, and large number of functional end-groups.^{15,16} Dendritic molecules exhibit a site-isolation effect of dendrons that creates a microenvironment preventing intermolecular interaction.¹⁷ The electronic behavior in dendrimers is still limited, although numerous groups have demonstrated the dielectric

performance of CuPc materials. More attention should be focused on development of hyperbranched CuPc polymers.

Herein we report a novel hyperbranched copper phthalocyanine (HBCuPc) synthesized from 4,4'-bis(3,4-dicyanophenoxy) biphenyl (BPh) and copper chloride (CuCl) in solution. The obtained stable and regular structure of the HBCuPc materials is attributed to the biphenyl segments, giving rise to good dielectric and thermal properties.

EXPERIMENTAL PROCEDURES

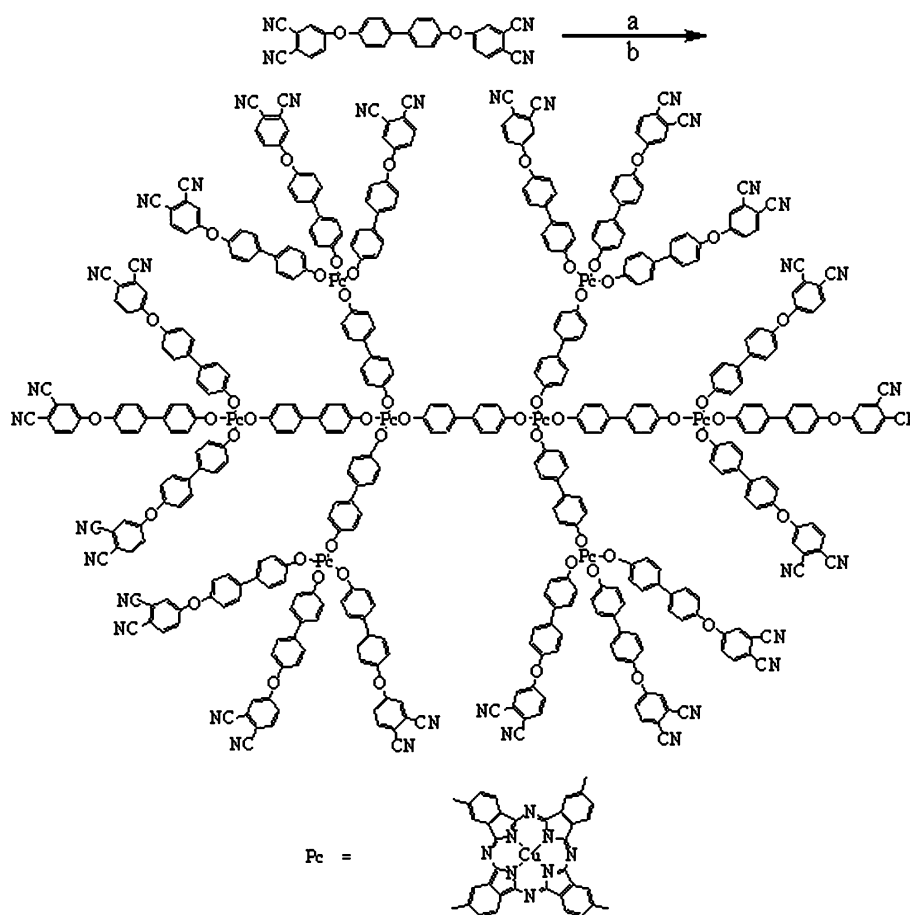
Materials

N,N-Dimethylacetamide (DMAC), *N*-methyl-2-pyrrolidinone (NMP), and copper chloride (CuCl) were obtained from Tianjin BODI chemicals. 4,4'-Bis(3,4-dicyanophenoxy) biphenyl (BPh) was prepared in our laboratory, according to Refs. 18, 19 with minor modification. All solvents were of reagent grade and were used without further purification.

Preparation of HBCuPc Oligomers

In a 250-mL three-necked round-bottomed flask equipped with a mechanical stirrer and refluxing

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Scheme 1. Synthetic route and structure of the branched HBCuPc (a: CuCl; b: DMAC, 160°C).

condenser, 8.80 g (20 mmol) BPh and 0.66 g (20/3 mmol) CuCl at a molar ratio of 3:1 were dissolved in 100 mL DMAC.⁷ The mixture was refluxed at 160°C for different reaction times (12 h, 24 h, and 36 h), then the crude product was poured into 1000 mL of deionized water with vigorous mechanical stirring. The resulting precipitate was collected by decompression filtration and dried at 80°C under vacuum. The resulting dark-green powder was further analyzed. On the other hand, the products with different concentrations were dissolved in NMP and kept overnight. Thus, pure HBCuPc materials based on biphenyl segments were obtained. The synthetic route and structure of the branched HBCuPc are shown in Scheme 1.

Characterization

Ultraviolet–visible (UV–Vis) spectra were recorded using a TU1800 spectrometer (Beijing Purkinje General Instrument Co., Ltd.). Fourier-transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR-8400S spectrometer in KBr pellets between 4000 cm^{-1} and 400 cm^{-1} in air. Nuclear magnetic resonance (¹H NMR) spectra were obtained using a Bruker AV400 spectrometer at a proton frequency of 400 MHz using dimethyl

sulfoxide (DMSO) as the solvent. The thermal curing behavior of the polymers was measured by using a TA Instruments modulated differential scanning calorimeter (DSC-Q100) with a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min. The thermal decompositions of the oligomers were determined by using a TA Instruments thermogravimetric analyzer (TGA-Q50) with a heating rate of 20°C/min under nitrogen atmosphere. Dielectric properties were measured by using a TH2819A precision LCR meter (Tonghui Electronic Co., Ltd.). The morphology of HBCuPc was observed by scanning electron microscopy (SEM, JSM-5900 LV) operating at 20 kV after gold sputtering.

RESULTS AND DISCUSSION

NMR, FTIR, and UV–Vis Spectra

The structures of the HBCuPc oligomers were verified by ¹H NMR and FTIR spectra. In Fig. 1a, the prominent resonances at 7.30 ppm to 8.13 ppm for the aromatic frequency correspond to hydrogen in the benzene ring. The ¹H NMR (400 MHz, DMSO) δ values are 8.13 ppm, 7.87 ppm, 7.82 ppm, 7.46 ppm, and 7.30 ppm. All resonances were assigned to H of benzene. There were four protons of

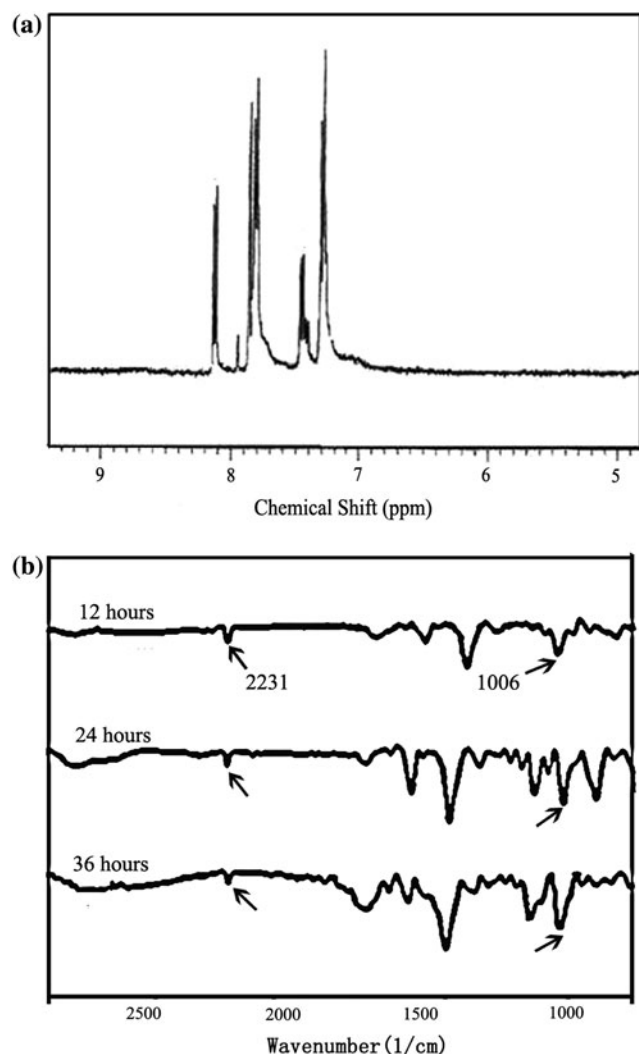


Fig. 1. (a) ^1H NMR and (b) FTIR spectra of HBCuPc oligomers.

the biphenyl segment in the monomer. The spectra of BPh and HBCuPc oligomers were similar, indicating that the reaction occurred at the end groups. Typical FTIR characteristic data were as follows: 2231 cm^{-1} (stretch, $-\text{CN}$), 1209 cm^{-1} (stretch, $\text{Ar}-\text{O}-\text{Ar}$), 885 cm^{-1} (bend, 1,2,4-substituted benzene), and 831 cm^{-1} (bend, 1,4-substituted benzene). The FTIR spectra of HBCuPc further confirmed the formation of HBCuPc, as shown in Fig. 1b. The characteristic cyano group peak at 2231 cm^{-1} obviously decreased with prolonged reaction time. On the other hand, a new characteristic peak at 1006 cm^{-1} was observed during polymerization of the cyano groups, indicating the formation of phthalocyanine rings.²⁰ The peak at 1006 cm^{-1} increased with prolonged time, suggesting an increase of the content of the CuPc unit in HBCuPc with higher degree of prepolymerization.

UV-visible (UV-Vis) spectroscopy of HBCuPc oligomers showed two strong characteristic absorption bands: a Soret (B) band at around 290 nm to

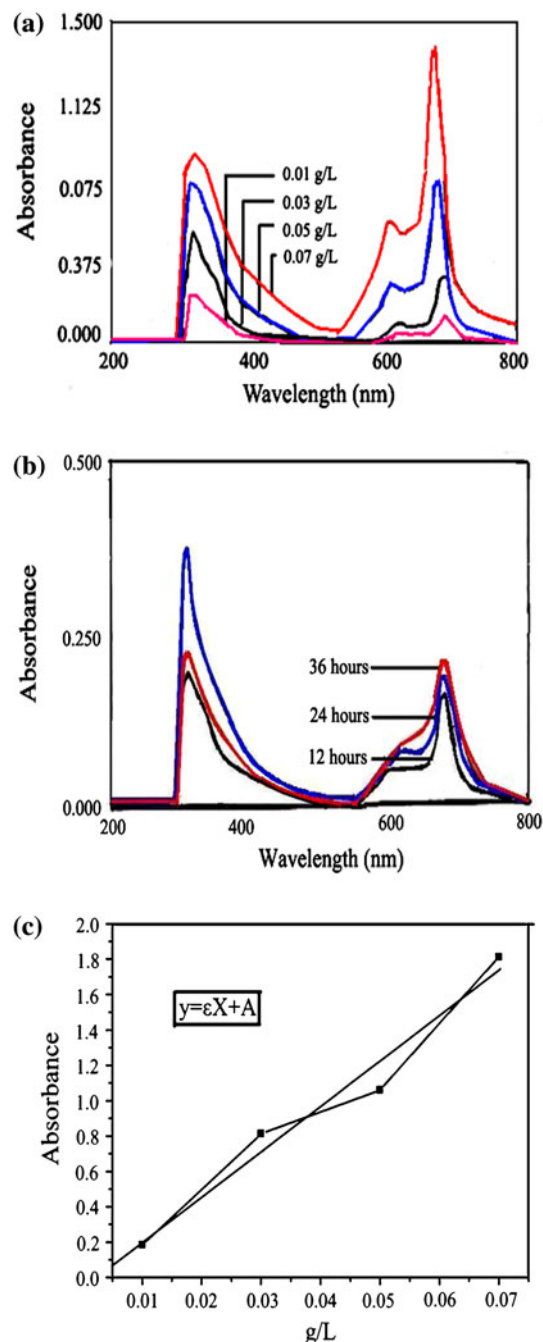


Fig. 2. UV-Vis spectra of HBCuPc oligomers for: (a) different concentrations (36 h) and (b) different reaction times. (c) ϵ of HBCuPc.

330 nm and a Q band at around 680 nm, which were due to excitation between the ground state $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ and $a_{1u}(\pi) \rightarrow e_g(\pi^*)$.³ Figure 2a shows the product spectra for 36 h reaction time with different concentrations. The increased intensity of the B band and the Q band was due to the higher concentration of HBCuPc. All the oligomers showed similar spectra and the increased intensity of the B band and the Q band with the prolonged reaction time (Fig. 2b). There was a relatively weak peak for this dendrimer, seen as a shoulder at

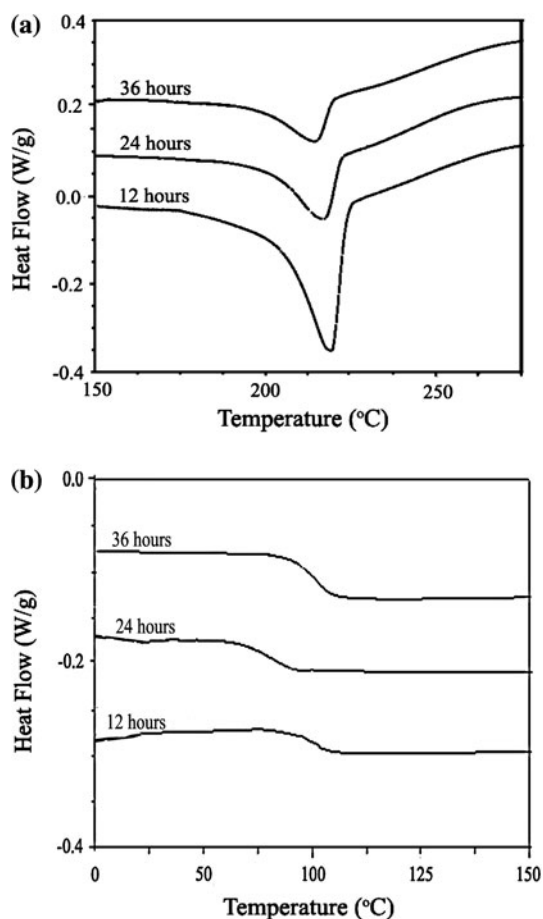


Fig. 3. DSC curves of HBCuPc: (a) T_{melt} and (b) T_g .

around 620 nm, which might be assigned to metal-to-ligand charge transfer.¹⁰

The content of the CuPc unit in HBCuPc of 12 h, 24 h, and 36 h oligomers were calculated as 8.76%, 14.92%, and 16.15%, respectively. The molar absorptivity (ϵ) value of the CuPc unit in this structure was calculated as $\epsilon = 172.19$. CuPc itself had ϵ of 281, and the ϵ value of HBCuPc oligomer was 15.08, 25.69, and 27.80, respectively, as obtained from the UV-Vis spectra (Fig. 2c). The UV-Vis spectra showed that the B and the Q absorption bands and the content of CuPc unit in HBCuPc all increased with prolonged reaction time. The number-average molecular weight (M_n) was about 1658, 2823, and 3056, respectively, whereas the weight-average molecular weight (M_w) was around 2174, 3702, and 4007, respectively.

Thermal Properties of HBCuPc Oligomers

The melting transitions (T_{melt}) occurred at 216.0°C, 211.3°C, and 210.9°C for the three oligomers of 12 h, 24 h and 36 h, as shown in Fig. 3a. These results indicate that T_{melt} decreases slightly with increasing reaction time. However, from Fig. 3b, all oligomers exhibited similar glass-transition temperature (T_g) around 100°C, indicating

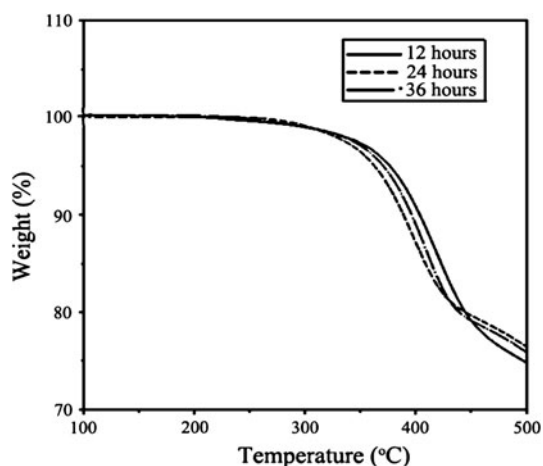


Fig. 4. Thermal decomposition behavior of HBCuPc under nitrogen atmosphere.

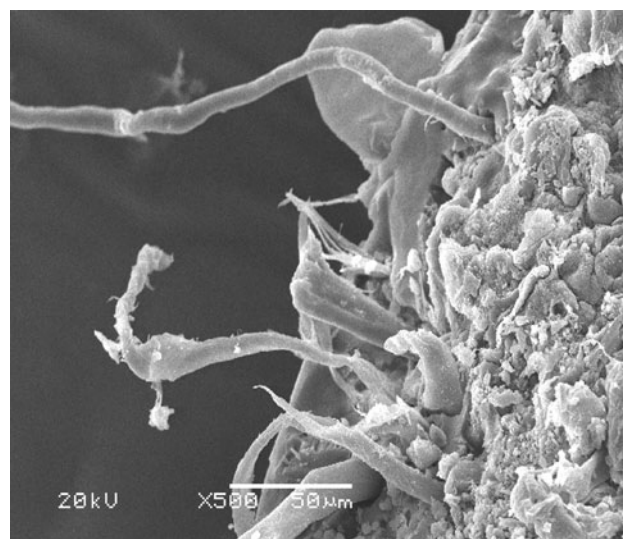


Fig. 5. SEM image of HBCuPc.

that increasing the reaction time had little effect on T_g . TGA curves of the HBCuPc oligomers are also plotted in Fig. 4. Overall, all HBCuPc oligomers possessed excellent thermal stability above 350°C and high char yields over 74% in nitrogen atmosphere at 500°C.

Morphologies of HBCuPc

Recently, the structures of phthalocyanine (Pc) materials made by self-assembly and self-organization methods has attracted great interest; for example, Nolte and coworkers reported a fiber structure of phthalocyanine that possessed one central phthalocyanine core as well as rod-like donor-acceptor phthalocyanine nanoaggregates.²¹ Figure 5 displays the SEM morphology of HBCuPc based on biphenyl segments. A kind of rigid rod of different lengths was found from the SEM micrograph, which was attributed to aggregation of CuPc

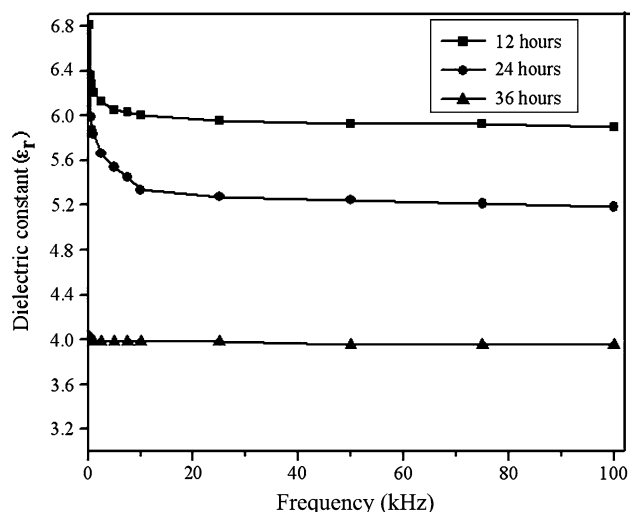


Fig. 6. Influence of frequency on the dielectric constant of HBCuPc.

particles.^{22,23} The hyperbranching and the tight packing between the phthalocyanine rings was due to strong π - π interaction, which contributed to the rod-like structure.

Dielectric Properties of HBCuPc Oligomers

The dielectric constant can be enhanced because of polar groups, such as cyano groups, which can result in dipole polarization. Hyperelectronic polarization dominated the large dielectric response, being due to the fast, long-range polaron delocalization within the giant conjugated molecule.⁷ In UV-Vis spectra with excitation around 620 nm, a weak peak was observed, confirming our assignment of metal-to-ligand charges.¹⁰ The metal-to-ligand charge transfer affected the polarization within the giant conjugated molecule, and the effect became greater with increasing prepolymerization. On the contrary, the metal-to-ligand charges increase with prolonged reaction time, which may weaken the polaron delocalization in the dendritic system.

Figure 6 shows constant-frequency dielectric curves for HBCuPc oligomers in the range from 0.25 kHz to 100 kHz. The HBCuPc had a dendritic-like structure consisting of four CN groups incorporated into the CuPc core. The content of CuPc unit in the HBCuPc oligomers increased with prolonged reaction time and fewer CN groups, in

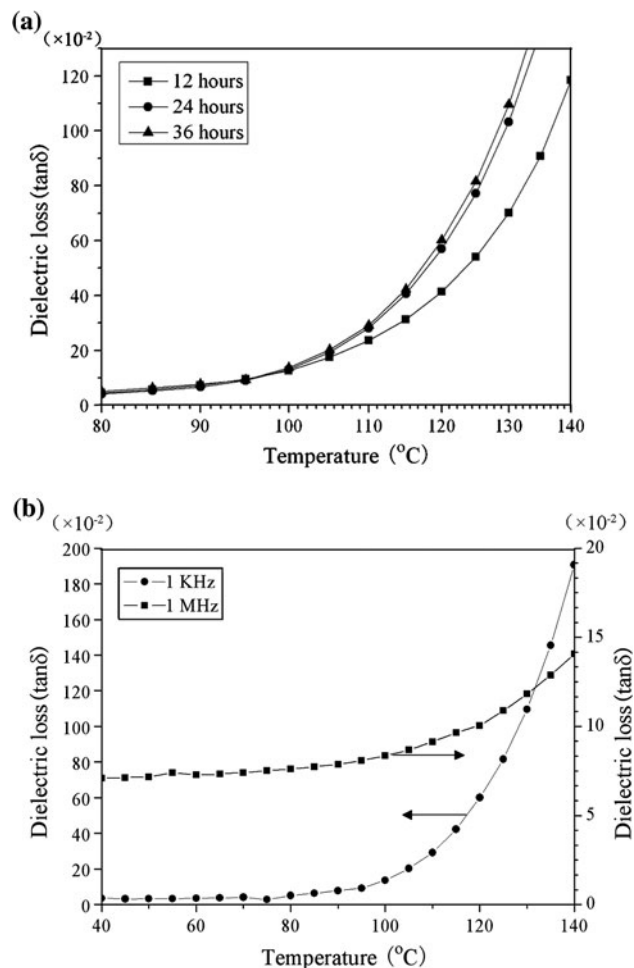


Fig. 7. Influence of temperature on the dielectric loss of 36 h HBCuPc oligomer for: (a) different reaction times at 1 kHz, and (b) different frequencies.

agreement with the UV-Vis results. The dielectric constant of the HBCuPc oligomers was in the range from 3.95 to 6.81, decreasing with increasing reaction time, which was attributed to fewer CN groups. The dielectric loss versus frequency data of the oligomers are summarized in Table I. The dielectric loss was small, in the range from 0.005 to 0.090, due to the effect of biphenyl segments and the hyperbranched rigid rod structure. The obtained HBCuPc oligomers possessed low dielectric loss and small dispersion of the dielectric constant with frequency.

Table I. Dielectric loss of HBCuPc oligomers

Reaction Time (h)	Frequency (kHz)								
	1.0	2.5	5.0	7.5	10.0	25	50	75	100
12	0.067	0.043	0.043	0.022	0.019	0.015	0.013	0.011	0.010
24	0.090	0.080	0.060	0.058	0.038	0.028	0.023	0.019	0.018
36	0.013	0.009	0.010	0.009	0.007	0.007	0.006	0.005	0.005

These results represent a major improvement over previous reports for Pc-related polymers and oligomers.^{9,24,25}

The dielectric loss versus temperature properties of the HBCuPc oligomers at 1 kHz are shown in Fig. 7a, with the different oligomers exhibiting similar curves from 40°C to 140°C. The dielectric loss of the HBCuPc oligomers shows good stability for temperatures up to 100°C but increases rapidly thereafter, which might be attributed to the glass transition. The molecular chain moves intensely because of the glass transition at around 100°C, which results in the increasing dielectric loss. Figure 7b shows the dielectric loss versus temperature curve for the 36 h oligomer at two different frequencies. It can be seen that the dielectric loss is much smaller at 1 MHz than at 1 kHz, increasing more slowly at the higher frequency.

CONCLUSIONS

A series of hyperbranched copper phthalocyanine (HBCuPc) oligomers based on biphenyl segments were synthesized using different reaction times. The materials exhibited good solubility, low dielectric loss, and good thermal stability. The structure of the HBCuPc oligomers was verified by FTIR and ¹H NMR spectra. The content of CuPc unit in the HBCuPc oligomers was improved by increasing the prepolymerization time from 12 h to 36 h. The dielectric loss was slightly influenced by temperature but remained stable below 100°C. Overall, the results indicate that the obtained novel HBCuPc materials have potential for applications as organic dielectric materials.

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