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COMMUNICATIONS

High Frequency Dielectric Response in a Branched Phthalocyanine

Meng Guo,[†] Xingzhong Yan,[†] Young Kwon,[‡] Teruaki Hayakawa,[‡] Masa-aki Kakimoto,[‡] and
Theodore Goodson III*,[†]

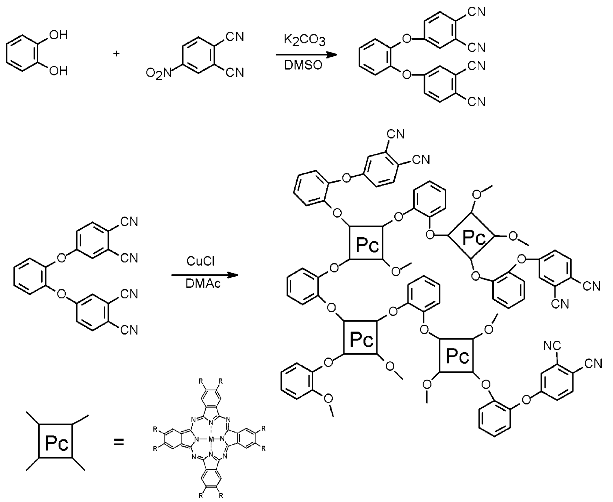
Department of Chemistry, The University of Michigan, 930 North University, Ann Arbor, Michigan 48109, and
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8550, Japan

Received May 30, 2006; E-mail: tgoodson@umich.edu

Recent interests in the use of novel polymeric materials for high dielectric constant effects have increased owing to their possible application in high-energy density and pulsed capacitors.[1,2] In particular, materials which demonstrate desired dielectric properties at high operational frequencies (>1 kHz) are highly sought after. Existing polymeric dielectrics, such as ceramic-polymers[3] and metal-polymeric composites,[4] typically exhibit a strong interfacial polarization (Maxwell−Wagner effect[5]), and this effect results in a strong dispersion of the dielectric constant. Polymeric materials mixed with phthalocyanine (Pc) tetramers have been reported with good dielectric response which is heavily related to a space charge effect.[6] However, the dielectric loss of these percolative systems is generally large,[3,4,6] and efforts are still necessary to improve the stability and flexibility of these systems. The use of Pc systems is an intriguing approach, and Pc polymer coated nanoparticles have been prepared and suggested as good candidates for dielectric applications.[7] Pc oligomers treated with base (KOH) have shown a large dielectric response at lower frequency, and this was explained under the Maxwell−Wagner−Sillars model.[8] While many of these reports present exciting avenues toward creating large dielectric responses in primarily organic materials, there has not been much attention to the intrinsic dielectric high-frequency response of all-organic systems. In this Communication, we report a strategy toward this aim utilizing an organic multichromophore structure such as a Pc dendritic system. Because of the long-range and fast polaron delocalization we find that a hyperelectronic polarization dominates the large dielectric response.

Shown in Scheme 1 is the phthalocyanine dendritic system investigated for strong dielectric response at high frequencies. The novel hyperbranched Pc was synthesized by a copper fusion technique consisting of 1,2-bis(3,4-dicyanophenoxy)benzene in dimethylacetamide (DMAC) at 160 °C. The extent of the cyclotetramerization reaction was monitored in real time by the increase of the absorption extinction coefficient of the products in comparison to the absorption of copper phthalocyanine complex. After extensive filtration and washing with MeOH, the products were dried, and the resulting dark blue crystals were further analyzed. The final structure of the branched Pc was determined by ^{1}H-NMR and UV−vis spectra (see Supporting Information).

Scheme 1. Synthetic Route and Structure of the Branched Pc Used in This Study



Measurements of the dielectric response up to 1 MHz were carried out with the pressure compressed pellets of the pristine material. Shown in Figure 1 is the dielectric response for a compressed pellet of the hyperbranched Pc illustrated in Scheme 1. The thickness of the compressed pellet shown in Figure 1 was $\sim$76 μm. As it can be seen from Figure 1, with this pellet a dielectric response of $\sim$46 is obtained even at frequencies of up to 1 MHz. This value is significant and is larger than that observed for the CuPc complex which was only 5.3 at 50 kHz.[1] It can also be noted in Figure 1 that the dispersion of the dielectric constant is very small. This result suggests a major improvement over what has been reported in the past with Pc related materials. For example, in the case of the oligomers of Pc, the dielectric dispersion is very large where the dielectric response drops by 3 orders of magnitude over a similar frequency range as that seen in the result of Figure 1.[8] Very small dispersion in an organic material has been also observed in Co(acac)$_2$-cured-expoy resin material; however, the dielectric response at these higher frequencies in this material was relatively small ($\sim$6 at 1 MHz).[3a] It has been suggested that for these systems such a small dispersion may be a result of the formation of large polar moieties.[3a] From our measurements of the previous similar systems, we find that this may also be the case for the hyperbranched Pc system where a long-range polaron delocalization in the branched structure gives rise to a small dispersion at high frequencies.[9,10]

Also observed in Figure 1 is a very low loss even at higher frequencies for this pristine dendritic Pc system. The loss is less than 0.01 at 1 MHz. This is an unprecedented result for such a low

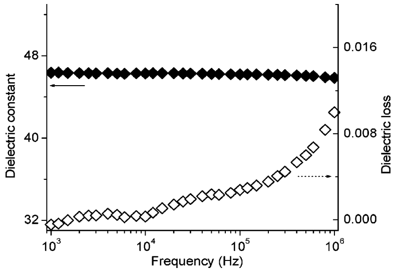


Figure 1. Dielectric dispersion curves of the hyperbranched Pc polymer compressed pellet with a thickness of 76 μm.

[†] The University of Michigan.
[‡] Tokyo Institute of Technology.

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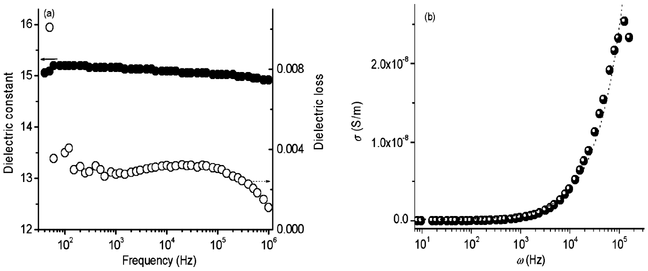

Figure 2. (a) Dielectric dispersion curves and (b) AC conductance of the branched Pc film.

loss, as previous results for Pc related polymers and oligomers had shown losses (tan δ) up to 0.7 for the polymer composite and above 1.0 for the Pc oligomers.[6,8,11] For the purpose of comparison, we also examined the dielectric properties of the Pc monomer: the dielectric constant was relatively small (~5) and the dielectric loss was high (up to 0.3). Although other results have been reported with the Pc oligomers and polymers, these results with the dendritic Pc system present a major improvement which we attribute to the long-range interactions in the hyperbranched structure.

To probe the transport mechanism which yields this impressive dielectric response in the dendritic Pc system, we carried out the analysis of the AC conductance. The AC conductance was analyzed by the expression given as $\sigma_{AC} = \epsilon_0 \epsilon_r \tan \delta\ \omega$, where ϵ_0 is the permittivity of the vacuum, ϵ_r is the real part of the dielectric constant, tan δ is the dielectric loss, and ω is the angular frequency. Measurements with the AC conductivity of the Pc samples showed a frequency dependent conductivity which could be fitted by a power law given as $\sigma_{AC} = A + B\omega^s$, where A and B are constants related to the DC (zero frequency conductivity) and s is a fitting parameter. The AC conductance of the pressure compressed pellet with a thickness of 76 μm showed the super-linear power law dependence with an s value of ~1.70. It has been suggested that the s parameter may give an indication of the charge transport mechanism in the system. For example, a value of the s parameter of 1.75 was obtained for a metallorgano Pc film.[12] Also, low temperature measurements of CuPc oligomers have found a superlinear dependence as well.[11] The explanation common to both of these cases in regards to the transport mechanism was heavily based on polaron tunneling in the system. However, for this situation the tunneling of polarons occurs on a relatively short length scale (short range interactions).[12] For the case of the compressed pellet sample of the dendritic Pc system, the contribution from a polaron tunneling mechanism is reasonable in describing the transport properties. It should be mentioned that in the case of the dendritic structure we have found that the interactions may extend over a number of repeat units and thus over larger length scales.[13] This effect may be sensitive to the macromolecular order exhibited in the dendritic system which may be a function of the fabrication (packing) of the solid-state system (compressed pellet or thin film).

To probe the importance of the morphology of the system once fabricated in the solid-state, we also carried out measurements of films of various thicknesses and concentrations of the branched Pc system. Shown in Figure 2 is the result for a film of the branched Pc coating on an Al substrate. This system also showed a very small dispersion and the dielectric constant was close to ~15 at 1 MHz. A very small dielectric loss (on the order of 0.001) was obtained at high frequencies (Figure 2a). Compared to TiO_2 functionalized polystyrene nanocomposites ($\epsilon_r = 6{\sim}10$),[14] the dielectric performance of the hyperbranched Pc films meets the stiff requirements for gate dielectrics and of organic transistor applications. Our measurements of different film's AC conductance showed no apparent thickness dependence. The AC conductance (σ_{AC}) of this pristine film exhibited a behavior which can be fitted by a power law with an s value in the range of ~0.8 (Figure 2b). This value for s suggests that the dominant mechanism of transport is a polaron hopping mechanism and may be related to the disordered dielectric effects in the system.[15] From our results on this and similar systems we have found that the polaron hopping can be relatively fast.[9] For example, with the use of time-resolved spectroscopy we have found that the hopping time can be as fast as ~1 ps.[9] Such a fast hopping would suggest a relatively strong long range interaction of the branched structure and this is an intrinsic effect. It is interesting to note that this was not the case for the pressure compressed pellet samples of the hyperbranched Pc, where a value of s greater than unity was obtained and this may be related to the fabrication procedure used to make the samples.

In conclusion, we have found a novel organic branched Pc dendrimer system which shows impressive dielectric properties with very low loss at high operational frequencies. Compared to percolative systems, this dendritic system shows very low loss at higher frequencies and a small dispersion, as well as improved stability and flexibility. Measurements were carried out with both pressure compressed pellets and thin films of the Pc dendrimer system. The mechanism for this impressive high-frequency response with relatively small dispersion is suggested to be due to a long-range polaron hopping mechanism accompanied by strong intramolecular interactions in the branched system.

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Supporting Information Available: Synthesis and characterization of the hyper-branched Pc polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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