Odd−Even Glass Transition Temperatures in Network-Forming Ionic Glass Homologue

Ke Yang,[†,‡] Madhusudan Tyagi,[§,⊥] Jeffrey S. Moore,*[,†,‡,∥] and Yang Zhang*[,‡,#]

[†]Beckman Institute for Advanced Science and Technology, [‡]Department of Materials Science and Engineering, [∥]Department of Chemistry, and [#]Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States

[§]NIST Center for Neutron Research, National Institute for Standards and Technology, Gaithersburg, Maryland 20899, United States,

[⊥]Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, United States

ⓢ *Supporting Information*

ABSTRACT: Odd−even effects, the non-monotonic dependency of physical properties on odd/even structural units, are widely observed in homologous series of crystalline materials. However, such alternation is not expected for molecular amorphous materials. Herein, we report the synthesis of a class of network-forming ionic glasses using multivalent ammonium cations and citrate anions. The glass transition temperatures of these amorphous solids show an alternating pattern with increasing backbone length. To understand the phenomenon's molecular origin, we performed incoherent elastic neutron scattering measurements of the nanosecond atomic dynamics. Our results suggest that the molecules' mobility, and thus the glass transition temperature, correlates with their structural symmetry.

In 1877, A. Baeyer discovered that the melting point of fatty acids does not exhibit a monotonic increase with increasing chain length.[1] Today it is textbook knowledge that even-membered *n*-alkanes and most of their α- and α,ω-substituents have higher melting temperatures than the odd-membered counterparts. Besides melting point,[2,3] odd−even effects of various systems have been shown in other properties such as fusion/sublimation enthalpy,[4] density,[5] mechanical properties,[6,7] surface properties,[8] and glass-forming abilities.[9] In general, "packing effects" are used to explain this alternation trend in crystalline materials. However, periodic packing does not exist in amorphous solids. Thus, the odd−even effect was not expected for molecular amorphous materials. For example, in most semicrystalline polymer homologues, although the melting temperatures (T_m) show odd−even alternation, the glass transition temperatures (T_g) only have a monotonic trend.[10−12] Here we report that the odd−even effect also exists in the fully amorphous state. We synthesized homologous network-forming ionic glasses (IGs) where organic multivalent cations and anions are connected primarily by electrostatic interactions. We found that the glass transition temperatures of this class of IGs show a nonmonotonic rise with increasing backbone chain length. We further investigated this odd−even effect by measuring the nanosecond hydrogen mean-squared displacement (MSD). The experiments described herein may be useful in guiding the design and the development of future

functional amorphous materials. In addition, influence of molecular symmetry on the glass transition is important for understanding and ultimately controlling dynamical slowing by tailoring the molecular architecture and intermolecular interactions.[13−15]

In conjunction with a project that investigates low-molecular-weight glasses as structural materials, we became interested in exploring glassy solids whereby network formation results from ion pairing. We followed established guidelines[16−21] for suppression of crystallization with multi-cationic and multi-anionic building blocks, such as by controlling the polarity, size of the molecules, and the nature of substituents.
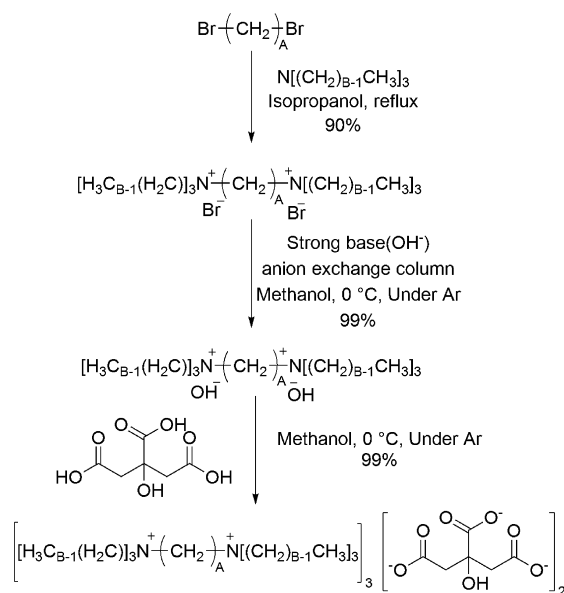
Our network-forming IGs were synthesized using diammonium cations and citrate anions. These materials were easily prepared by reacting a α,ω-dibromoalkane with a trialkylamine. The bromide counterion was then replaced with hydroxide using an anion exchange column. *In situ* reaction with citric acid (or other polyacids) produced the desired products and water. The materials were freeze-dried for 2 days (Scheme 1).[22]

The amorphous nature of IGs was determined by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). XRD spectra were collected below the glass transition temperature (Figure 1b). The peak assignments in XRD were explained in literature for molten ammonium ions.[23] The first peak at $q = 0.7$ Å^{-1} is related to the form factor of the electron density around the nitrogen atom in diammonium cation with alkyl spikes, and the second peak around $q = 1.7$ Å^{-1} is related to first-neighbor interactions.[24] The glass transition temperatures of various IGs were measured using two independent methods: direct measurement by DSC (Figure 1c) and the crossover point of the storage modulus (G') and loss modulus (G'') under dynamic loading (1 Hz) by rheology (Figure S2).

Increasing the spike length decreases the glass transition temperature (Table S1). Both electrostatic and van der Waals forces likely influence the phase behavior. Because electrostatic force is inversely proportional to the square of distance, increasing the length of side chains increases the steric hindrance between positive and negative charges. As a result, even though the van der Waals forces between segments may increase, glass transition temperature drops due to weaker

Scheme 1. Synthesis Route for Network-Forming Ionic Glass[a]

$$Br-(CH_2)_A-Br$$

N[(CH$_2$)$_{B-1}$CH$_3$]$_3$
Isopropanol, reflux
90%

$$[H_3C_{B-1}(H_2C)]_3N^+-(CH_2)_A-{}^+N[(CH_2)_{B-1}CH_3]_3$$
$$\overset{-}{Br}\qquad\overset{-}{Br}$$

Strong base(OH⁻)
anion exchange column
Methanol, 0 °C, Under Ar
99%

$$[H_3C_{B-1}(H_2C)]_3N^+-(CH_2)_A-{}^+N[(CH_2)_{B-1}CH_3]_3$$
$$\overset{-}{OH}\qquad\overset{-}{OH}$$

Methanol, 0 °C, Under Ar
99%

$$\left[[H_3C_{B-1}(H_2C)]_3N^+-(CH_2)_A-{}^+N[(CH_2)_{B-1}CH_3]_3\right]_3\ \left[{}^-O_2C\cdots CO_2^-\right]_2$$

[a]Naming: "IG #A-#B", #A is the backbone "spacer" methylene unit number and #B is the side chain "spikes" methylene/methyl unit number.
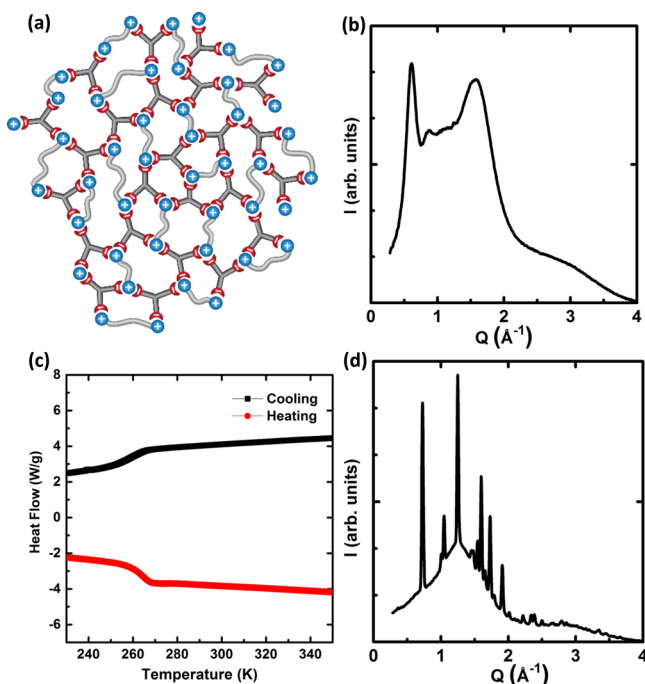

Figure 1. (a) Simplified 2-D schematic depiction of interconnected polyionic glass (spikes group in cations are not shown). (b) Representative powder XRD pattern of IG. (c) Representative DSC curve of IG. (d) Powder XRD pattern of semicrystalline material observed for ammonium cations having small values of *B*.

electrostatic interactions. Based on this observation, side-chain length was reduced in order to increase the glass transition temperature. However, no glassy solids were obtained when the side chains were reduced to a methyl or ethyl group. When the side chains are reduced, the cations and anions can get closer, resulting in stronger electrostatic attraction that leads to stable

nanocrystals. Instead, opaque semicrystal samples were obtained (Figure 1d). These results demonstrate that the ionic interaction strength can be fine-tuned by tailoring the structure of the building blocks as long as the spikes are long enough to frustrate crystallization.

Investigating the dependence of T_g on spacer length, the overall trend exhibits a peak shape (Figure 2a). The drop in T_g
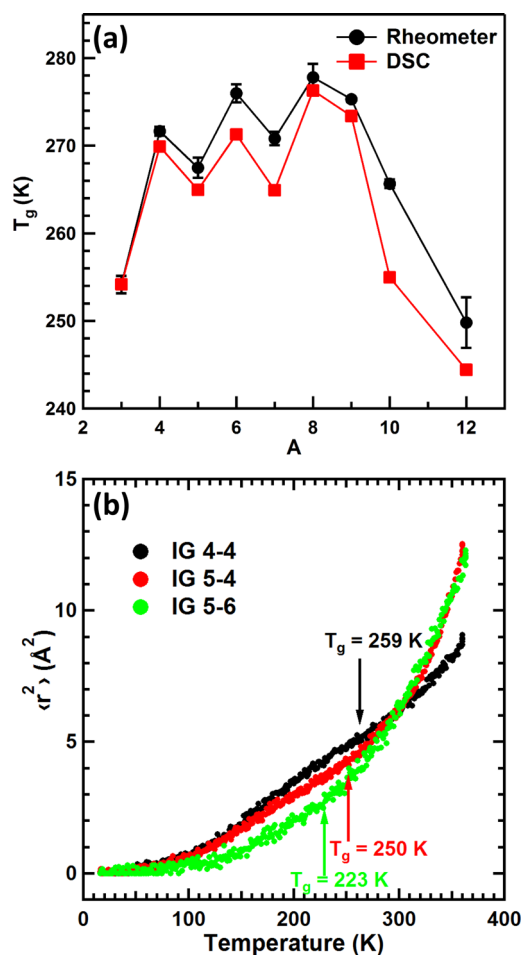
Figure 2. (a) Odd−even dependence of the glass transition temperatures (determined by both rheology and DSC) of IGs by varying spacer alkyl chain length (IG A-3). (b) Nanosecond hydrogen mean-squared displacement of three selective IGs extracted from elastic incoherent neutron scattering experiments. Error bars represent one standard deviation. The glass transition temperatures in panel (b) are determined by DSC.

for long spacer lengths is explained by the competition between the electrostatic and van der Waals forces. An unexpected odd−even effect was observed in the spacer length study. IGs with an even number of methylene groups consistently have higher T_g than the odd-numbered IGs. The magnitude of the odd−even effect varies from system to system. For our IGs, the maximum difference in neighboring T_g is 15K. To compare, for *n*-alkane, the maximum difference of neighboring T_m is about 30 K;[2] for some polyesters, it ranges from 15 to 100 K;[6,11,25] for α,ω-diamides, it can be as large as 130 K.[4] The alternation amplitude decreases with longer chains, which is consistent with *n*-alkanes and its derivates.[2,4] When *n* > 9, the odd−even effect was not observed suggesting the effect from weaker ionic interaction per molecular volume becomes more prominent. To

the best of our knowledge, this is the first time such an odd–even effect on T_g has been observed in ionic networks.

Unlike crystallization, glass transition is not a thermodynamic transition, but rather a dynamic slowing-down process. Therefore, packing effects in crystalline materials cannot be applied directly to amorphous solids. To understand the odd–even phenomenon from the dynamic point of view, we measured the atomistic dynamics of IGs using incoherent elastic neutron scattering (IENS). IENS probes the effective Debye–Waller factor, $\exp(-(1/6)\langle r^2 \rangle Q^2)$, averaged over the nanosecond time resolution window, which directly yields the hydrogen MSD.[26] For our IG system, most of the hydrogen atoms are in nonspherical cations, so the MSD would reflect mostly the cations' behavior. Detailed data analysis can be found in the Supporting Information (Figure S3). Three samples (IG 4-4, IG 5-4, and IG 5-6) were chosen in order to decouple the contributions to MSD from the side chains and backbone. As shown in Figure 2b, a typical IG's nanosecond hydrogen MSD as a function of temperature can be divided into three regimes: (i) Below 100 K, MSD shows pure harmonic behavior, almost all relaxational degrees of freedom freeze. (ii) From 100 to 250 K, anharmonic motions start contributing. IG 4-4 and IG 5-4, with the same spike length, show similar temperature dependence, while IG 5-6, with longer hexyl side chain, exhibits slower motions. This contrast suggests that the motion of the IG alkyl side chain (spikes group) dominates in this temperature range. In comparison, the backbone is primarily immobile in this regime, as the ionic cross-links behave like "anchors" and restrict the backbone diffusional movement. (iii) Above 250 K, which is close to the glass transition temperature, the hydrogen MSDs increase dramatically. IG 5-4 and IG 5-6, with the same backbone length, behave almost identically, while IG 4-4 moves much slower. Therefore, we can reasonably conclude that the nanosecond molecular motions of IG are determined by the backbone rather than the side chain in this temperature range.

Comparing IG 4-4 and IG 5-4, which have the same number of spike groups but adjacent numbers of spacer groups, the main difference of their MSD lies in regime (iii) ($T > T_g$), where IG 4-4 molecules exhibit considerably slower motions compared to IG 5-4. This measurement of the molecular mobility explains why IG 4-4 has a higher T_g than its odd-membered counterpart. Indeed, the mobility of the molecules is influenced by their structural symmetry, central symmetry for even-membered IG and mirror symmetry for odd-membered IG, which ultimately determines the configurational entropy of the system and thus affects the glass transition temperature. Another interesting feature of the MSD plot is that all three curves seem to have a common crossover point around 300 K, which is under current investigation.

In summary, an anomalous glass transition temperature odd–even effect was observed in network-forming ionic glasses. Measurements of mean-squared displacement reveal the discrete mobility of side chain and backbone at different temperatures. Comparison of odd- and even-membered MSD plots shows the effect is associated with molecular mobility differences. We demonstrated here that the ionic strength and mobility can be adjusted in a homologous series. The strategy provides an opportunity to fine-tune the properties of macroscopic materials in the area of supramolecular chemistry and molecular recognition. This system, with all its versatility, is a potential model system for the study of glasses and liquids.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Syntheses, DSC and rheology data, and fitting of elastic neutron scattering data to get hydrogen MSD. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

jsmoore@uiuc.edu
zhyang@illinois.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Baeyer, A. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 1286.
(2) Cvd, M.; Kodas, E. T. T.; Boese, R.; Weiss, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 988.
(3) Morishige, K.; Kato, T. *J. Chem. Phys.* **1999**, *111*, 7095.
(4) Badea, E.; Della Gatta, G.; D'Angelo, D.; Brunetti, B.; Rečková, Z. *J. Chem. Thermodyn.* **2006**, *38*, 1546.
(5) Mukherjee, G.; Biradha, K. *Cryst. Growth Des.* **2011**, *11*, 924.
(6) Jeong, Y. G.; Jo, W. H.; Lee, S. C. *Polymer.* **2004**, *45*, 3321.
(7) Shiotani, A.; Kohda, M. *J. Appl. Polym. Sci.* **1999**, *74*, 2404.
(8) Tao, F.; Bernasek, S. L. *Chem. Rev.* **2007**, *107*, 1408.
(9) Imae, I.; Kawakami, Y. *Chem. Lett.* **2005**, *34*, 290.
(10) Craig, A. a.; Imrie, C. T. *Macromolecules* **1999**, *32*, 6215.
(11) Mary, L. J. F.; Kannan, P. *J. Polym. Sci., Part A Polym. Chem* **1999**, *37*, 1755.
(12) In some rare cases, where odd–even effects were observed in T_g, crystal domains act as fillers and physical cross-links. The alternation is related with packing effects in crystal: (a) Konstandakopoulou, F. D.; Gravalos, K. G.; Kallitsis, J. K. *Macromolecules* **1998**, *31*, 5264. (b) Serrano, P. J. M.; Thoss, E.; Gaymans, R. *Polymer* **1997**, *38*, 3893. (c) Mather, P. T.; Jeon, H. G.; Han, C. D.; Chang, S. *Macromolecules* **2002**, *35*, 1326.
(13) Debenedetti, P. G.; Stillinger, F. H. *Nature* **2001**, *410*, 259.
(14) Chandler, D. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 15111.
(15) Angell, C. a. *Science* **1995**, *267*, 1924.
(16) Katsuma, B. K.; Shirota, Y. *Adv. Mater.* **1998**, *10*, 223.
(17) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.
(18) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.
(19) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75.
(20) Dai, J.; Chang, S.; Hamad, A.; Yang, D. *Chem. Mater.* **2006**, *18*, 3404.
(21) Tanino, T.; Yoshikawa, S.; Ujike, T.; Nagahama, D.; Moriwaki, K.; Takahashi, T.; Kotani, Y.; Nakano, H.; Shirota, Y. *J. Mater. Chem.* **2007**, *17*, 4953.
(22) Bromide elemental analysis was done to confirm the conversion of ion exchange. Bromide content in final products was <100 ppm. The water content was determined by Karl Fischer titration and was <2000 ppm.
(23) Zheng, W.; Mohammed, A.; Hines, L. G.; Xiao, D.; Martinez, O. J.; Bartsch, R. a; Simon, S. L.; Russina, O.; Triolo, A.; Quitevis, E. L. *J. Phys. Chem. B* **2011**, *115*, 6572.
(24) Minoru Mizuhata; Masanori Maekawa, S. D. *ECS Trans.* **2007**, *3*, 89.

(25) Hägele, C.; Wuckert, E.; Laschat, S.; Giesselmann, F. *Chemphyschem* **2009**, *10*, 1291–.

(26) Wolfgang Doster; Stephen Cusack, W. P. *Nature* **1989**, *337*, 754.