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First Clear-Cut Experimental Evidence of a Glass Transition in a Polymer with Intrinsic Microporosity: PIM-1

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Abstract

© 2018 American Chemical Society. Polymers with intrinsic microporosity (PIMs) represent a novel, innovative class of materials with great potential in various applications from high-performance gas-separation membranes to electronic devices. Here, for the first time, for PIM-1, as the archetypal PIM, fast scanning calorimetry provides definitive evidence of a glass transition (Tg = 715 K, heating rate 3 × 104 K/s) by decoupling the time scales responsible for glass transition and decomposition. Because the rigid molecular structure of PIM-1 prevents any conformational changes, small-scale bend and flex fluctuations must be considered the origin of its glass transition. This result has strong implications for the fundamental understanding of the glass transition and for the physical aging of PIMs and other complex polymers, both topical problems of materials science.

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References

[1] Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. Chem. Commun. 2004, 0, 230-231, 10.1039/b311764b

[2] Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. An efficient polymer molecular sieve for membrane gas separations. Science 2013, 339, 303-307, 10.1126/science.1228032

[3] Yin, Y.; Guiver, M. D. Microporous polymers: ultrapermeable membranes. Nat. Mater. 2017, 16, 880-881, 10.1038/nmat4961

[4] McKeown, N. B.; Budd, P. M. Exploitation of intrinsic microporosity in polymer-based materials. Macromolecules 2010, 43, 5163-5176, 10.1021/ma1006396

[5] McDermott, A. G.; Larsen, G. S.; Budd, P. M.; Colina, C. M.; Runt, J. Structural characterization of a polymer of intrinsic microporosity: X-ray scattering with interpretation enhanced by molecular dynamics simulations. Macromolecules 2011, 44, 14-16, 10.1021/ma1024945

[6] Larsen, G. S.; Lin, P.; Hart, K. E.; Colina, C. M. Molecular simulations of PIM-1-like polymers of intrinsic microporosity. Macromolecules 2011, 44, 6944-6951, 10.1021/ma200345v

[7] Anderson, P. W. Through the glass lightly. Science 1995, 267, 1615-1616, 10.1126/science.267.5204.1615-e

[8] Angell, C. A. Formation of glasses from liquids and biopolymers. Science 1995, 267, 1924-1935, 10.1126/science.267.5206.1924

[9] Debenedetti, P. G.; Stillinger, F. H. Supercooled liquids and the glass transition. Nature 2001, 410, 259-267, 10.1038/35065704

[10] Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. Poly[1-(trimethylsilyl)-1-propyne] and related polymers: synthesis, properties and functions. Prog. Polym. Sci. 2001, 26, 721-798, 10.1016/S0079-6700(01)00008-9

[11] Swaidan, R.; Ghanem, B.; Pinnau, I. Fine-tuned intrinsically ultramicroporous polymers redefine the permeability/selectivity upper bounds of membrane-based air and hydrogen separations. ACS Macro Lett. 2015, 4, 947-951, 10.1021/acsmacrolett.5b00512

[12] Gupta, B. K.; Kedawat, G.; Kumar, P.; Rafiee, M. A.; Tyagi, P.; Srivastava, R.; Ajayan, P. M. An n-type, new emerging luminescent polybenzodioxane polymer for application in solution-processed green emitting OLEDs. J. Mater. Chem. C 2015, 3, 2568-2574, 10.1039/C4TC02581D

[13] Wang, Q.; Jin, J.; Wu, X.; Ma, G.; Yang, J.; Wen, Z. A shuttle effect free lithium sulfur battery based on a hybrid electrolyte. Phys. Chem. Chem. Phys. 2014, 16, 21225-21229, 10.1039/C4CP03694H

[14] He, D.; Rauwel, E.; Malpass-Evans, R.; Carta, M.; McKeown, N. B.; Gorle, D. B.; Anbu Kulandainathan, M.; Marken, F. Redox reactivity at silver microparticle-glassy carbon contacts under a coating of polymer of intrinsic microporosity (PIM). J. Solid State Electrochem. 2017, 21, 2141-2146, 10.1007/s10008-017-3534-2

[15] Konnertz, N.; Ding, Y.; Harrison, J. W.; Budd, P. M.; Schönhals, A.; Böhning, M. Molecular mobility of the high performance membrane polymer PIM-1 as investigated by dielectric spectroscopy. ACS Macro Lett. 2016, 5, 528-532, 10.1021/acsmacrolett.6b00209

[16] Ward, A. L.; Doris, S. E.; Li, L.; Hughes, M. A., Jr.; Qu, X.; Persson, K. A.; Helms, B. A. Materials genomics screens for adaptive ion transport behavior by redox-switchable microporous polymer membranes in lithium-sulfur batteries. ACS Cent. Sci. 2017, 3, 399-406, 10.1021/acscentsci.7b00012

[17] Ravi, S.; Gopi, C. V. V; Kim, H. Enhanced electrochemical capacitance of polyimidazole coated covellite CuS dispersed CNT composite materials for application in supercapacitors. Dalton Trans. 2016, 45, 12362-12371, 10.1039/C6DT01664B

[18] Hodge, I. M. Physical aging in polymer glasses. Science 1995, 267, 1945-1947, 10.1126/science.267.5206.1945

[19] Swaidan, R.; Ghanem, B.; Litwiller, E.; Pinnau, I. Physical aging, plasticization and their effects on gas permeation in "rigid" polymers of intrinsic microporosity. Macromolecules 2015, 48, 6553-6561, 10.1021/acs.macromol.5b01581

[20] Yin, H.; Chapala, P.; Bermeshev, M.; Schönhals, A.; Böhning, M. Molecular mobility and physical aging of a highly permeable glassy polynorbornene as revealed by dielectric spectroscopy. ACS Macro Lett. 2017, 6, 813-818, 10.1021/acsmacrolett.7b00456

[21] McDermott, A. G.; Budd, P. M.; McKeown, N. B.; Colina, C. M.; Runt, J. Physical aging of polymers of intrinsic microporosity: a SAXS/WAXS study. J. Mater. Chem. A 2014, 2, 11742-11752, 10.1039/C4TA02165G

[22] Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wang, D. Solution-processed, organophilic membrane derived from a polymer of intrinsic microporosity. Adv. Mater. 2004, 16, 456-459, 10.1002/adma.200306053

[23] Staiger, C. L.; Pas, S. J.; Hill, A. J.; Cornelius, C. J. Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer. Chem. Mater. 2008, 20, 2606-2608, 10.1021/cm071722t

[24] Heuchel, M.; Fritsch, D.; Budd, P. M.; McKeown, N. B.; Hofmann, D. Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1). J. Membr. Sci. 2008, 318, 84-99, 10.1016/j.memsci.2008.02.038

[25] Golzar, K.; Modarress, H.; Amjad-Iranagh, S. Effect of pristine and functionalized single- and multi-walled carbon nanotubes on CO2 separation of mixed matrix membranes based on polymers of intrinsic microporosity (PIM-1): a molecular dynamics simulation study. J. Mol. Model. 2017, 23, 266, 10.1007/s00894-017-3436-3

[26] Schick, C.; Mathot, V. Fast Scanning Calorimetry; Springer International Publishing: New York, 2016.

[27] Schawe, J. E. K. Vitrification in a wide cooling rate range: The relations between cooling rate, relaxation time, transition width, and fragility. J. Chem. Phys. 2014, 141, 184905, 10.1063/1.4900961

[28] Adam, G.; Gibbs, J. H. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. J. Chem. Phys. 1965, 43, 139-146, 10.1063/1.1696442

[29] Donth, E. The glass transition: relaxation dynamics in liquids and disordered materials; Springer: Berlin, Germany, 2001.

[30] Dalle-Ferrier, C.; Kisliuk, A.; Hong, L.; Carini, G., Jr.; Carini, G.; D'Angelo, G.; Alba-Simionesco, C.; Novikov, V. N.; Sokolov, A. P. Why many polymers are so fragile: a new perspective. J. Chem. Phys. 2016, 145, 154901, 10.1063/1.4964362

[31] Boucher, V. M.; Cangialosi, D.; Alegría, A.; Colmenero, J. Enthalpy recovery in nanometer to micrometer thick polystyrene films. Macromolecules 2012, 45, 5296-5306, 10.1021/ma300622k

[32] Cangialosi, D.; Alegria, A.; Colmenero, J. Cooling rate dependent glass transition in thin films and in bulk. In Fast Scanning Calorimetry; Schick, C., Mathot, V., Eds.; Springer International Publishing; New York, 2016; pp 403-431.

[33] Martin, J.; Stingelin, N.; Cangialosi, D. Direct calorimetric observation of the rigid amorphous fraction in a semiconducting polymer. J. Phys. Chem. Lett. 2018, 9, 990-995, 10.1021/acs.jpclett.7b03110

[34] Monnier, X.; Saiter, A.; Dargent, E. Vitrification of PLA by fast scanning calorimetry: towards unique glass above critical cooling rate?. Thermochim. Acta 2017, 658, 47-54, 10.1016/j.tca.2017.10.019

[35] Rose, I.; Bezzu, C. G.; Carta, M.; Comesana-Gandara, B.; Lasseuguette, E.; Ferrari, M. C.; Bernardo, P.; Clarizia, G.; Fuoco, A.; Jansen, J. C.; Hart, K. E.; Liyana-Arachchi, T. P.; Colina, C. M.; McKeown, N. B. Polymer ultrapermeability from the inefficient packing of 2D chains. Nat. Mater. 2017, 16, 932-937, 10.1038/nmat4939

[36] Chapala, P.; Bermeshev, M.; Starannikova, L.; Shantarovich, V.; Gavrilova, N.; Lakhtin, V.; Yampolskii, Y.; Finkelshtein, E. S. Synthesis and gas-transport properties of novel copolymers based on tricyclononenes containing one and three MeSi-groups. Macromol. Chem. Phys. 2017, 218, 1600385, 10.1002/macp.201600385

[37] Ma, X. H.; Ghanem, B.; Salines, O.; Litwiller, E.; Pinnau, I. Synthesis and effect of physical aging on gas transport properties of a microporous polyimide derived from a novel spirobifluorene-based dianhydride. ACS Macro Lett. 2015, 4, 231-235, 10.1021/acsmacrolett.5b00009

[38] Zorn, R.; Yin, H.; Lohstroh, W.; Harrison, W.; Budd, P. M.; Pauw, B. R.; Böhning, M.; Schönhals, A. Anomalies in the low frequency vibrational density of states for a polymer with intrinsic microporosity-the Boson peak of PIM-1. Phys. Chem. Chem. Phys. 2018, 20, 1355-1363, 10.1039/C7CP07141H

[39] Zhuravlev, E.; Schick, C. Fast scanning power compensated differential scanning nano-calorimeter: 1. The device. Thermochim. Acta 2010, 505, 1-13, 10.1016/j.tca.2010.03.019