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Effects of Intermolecular Forces on the Glass Transition of Polymers

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The glass transition temperature, T_g, of an amorphous or a semicrystalline polymer is the most important material parameter that defines its temperature-dependent mechanical and other physical properties.[1–6] Although the true origin of the glass transition phenomenon, i.e., whether it is thermodynamic or kinetic, remains unclear;[2] experimental facts of the glass transition are commonly explained in terms of the rapid molecular motion of polymer chains above T_g and the substantially reduced chain mobility below T_g.[1–6] Above the T_g, a polymeric material can thus flow and be stretched or shaped into useful forms. Since the modulus and other physical properties of a polymer can change by orders of magnitude at T_g, this material parameter often sets the upper bound on use temperature in applications.[1–6] The value of the T_g is thought to be determined by such factors as the chain stiffness (or flexibility), molecular symmetry, the presence of a side group (and its size and flexibility), molecular weight, chain branching, cross-linking, and intermolecular forces.[1–6] We report here a direct experimental observation of the effects of intermolecular interactions on the T_g of diverse polymers and show that alleviation of such intermolecular forces causes a dramatic shift of the T_g to a lower temperature by as much as 470 °C in some cases. Complexation-induced alleviation of the intermolecular forces in superstrong, high-modulus, high-temperature polymers, such as poly(*p*-phenylenebenzobisthiazole), turns them into rubbery materials at barely above room temperature (30 °C). Restoration of the intermolecular forces by decomplexation restores the materials to their pristine stiffness and properties. These results suggest that intermolecular forces in polymers can have a more dominant influence on the T_g than previously thought.

It is well known that intermolecular interactions, such as hydrogen bonding, dispersion (van der Waals) forces, dipole–dipole forces, and induction forces, determine the equilibrium structure and properties of synthetic and biological polymers,[4,5] and indeed all condensed matter.[7] Among the many polymer properties that depend on intermolecular forces or cohesive energy are mechanical, surface and interfacial, thermophysical (e.g., T_g, T_m, thermal stability, crystallinity), optical, solubility, and miscibility properties.[5] We recently introduced the approach of reversible Lewis acid–base coordination complexation of polymers[8–15] as a way of probing the effects of intermolecular forces in polymers.[8–10,13–15] The approach is based on the fact that most synthetic and naturally occurring polymers contain heteroatoms (ligands) such as oxygen, sulfur, nitrogen, or phosphorus with nonbonding electron pairs (Lewis base sites) in the main chain or side groups.[4–6] Complexation of such polymer ligands with Lewis acids such as metal halides ($AlCl_3$, BCl_3, BF_3, $FeCl_3$, $GaCl_3$) gives coordination complexes with much weaker intermolecular attractions.[15–17] The structure and properties of the complexes are compared to those of the pure polymers to infer effects of intermolecular interactions. Furthermore, a suitable choice of a stronger Lewis base than the polymer ligands can reverse the complexation, regenerating the pure polymers.[9,10,14,15] We have already used this approach to examine the effects of intermolecular interactions on the solubility,[8–15] polymer–polymer miscibility of several polymers, and preliminary observations of the effects of complexation on thermal properties, including the T_g.[14]

Several polymers with strong intermolecular interactions, whose molecular structures are shown in Figure 1, were investigated: an aliphatic semicrystalline polyamide (nylon 66, T_g = 55 °C, T_m = 260 °C); an amorphous aromatic polyamide, poly(trimethylhexamethyleneterephthalamide) (PTMHT, T_g = 153 °C); a rigid-rod, high-modulus, high-strength polymer poly(*p*-phenylenebenzobisthiazole) (PBZT); and the semiladder and ladder poly(benzimidazole–benzophenanthrolines) (BBB, BBL). The dominant intermolecular interaction in the polyamides is hydrogen bonding.[15] The conjugated polymers PBZT, BBB, and BBL are high-temperature materials[6,9,10] with thermal stability in excess of 600 °C in air and 700 °C in nitrogen. PBZT retains its modulus and mechanical strength to at least 650 °C.[18] PBZT can be expected to have a higher T_g than its nonfused analogue, poly(2,6-benzothiazolediyl-6,2-benzothiazolediyl-1,3-phenylene), which has a T_g of 495 °C.[19] It was concluded from mechanical measurements that the T_g of BBB was ≥500 °C.[20] The T_g of BBL has been estimated to be ≥500 °C.[6] Our own prior differential scanning calorimetry (DSC) studies of PBZT, BBB, and BBL did not reveal a glass transition up to 500 °C.[9,10] We therefore take 500 °C as the best and conservative estimate of the T_g of either PBZT, BBB, or BBL. The strong intermolecular interactions in PBZT, BBB, and BBL have been theoretically shown to be van der Waals forces.[21,22]

The idealized structures of the corresponding Lewis acid coordination complexes of the polymers, using gallium(III) chloride as the Lewis acid, are also shown in Figure 1. The detailed preparation of these complexes in nitromethane solutions was described previously.[9,10,14] The solid complexes were obtained as films cast on glass followed by slow evaporation of nitromethane in vacuum at 65 °C or in nitrogen at 50–60 °C. Decomplexation to recover the pure polymers from the complexes was accomplished by immersion of the solid complexes in water or methanol overnight.

The DSC thermograms of the polyamides and their $GaCl_3$ complexes are shown in Figure 2. The measured T_gs for the pure nylon 66 and pure PTMHT were 55 and 153 °C, respectively. The observed T_gs of $GaCl_3$–nylon 66 and $GaCl_3$–PTMHT were −4 and 10 °C, respectively. The polyamide complexes were stretchable rubbery materials at room temperature. The decrease in T_g on complexation of nylon 66 and PTMHT, 59 and 143 °C, respectively, is due to the scission of the intermolecular $N{-}H\cdots O{=}C$ hydrogen bonds since the carbonyl oxygens are the complexation sites.[15] The difference between the T_gs of the complexes is only 14 °C, compared with a difference of almost 100 °C in the pure polymers. Therefore, although in the pure PTMHT the aromatic group in the polymer backbone significantly reduces chain mobility and so increases T_g, this effect is largely negated in the complexes by elimination of intermolecular hydrogen bonding. On decomplexation, and hence restoration of hydrogen bonding,[15] the T_gs of the recovered pure polyamides were identical to the pristine values (55 and 153 °C).

Figure 3 shows the DSC thermograms of PBZT, BBB, BBL, and their $GaCl_3$ complexes. The observed T_gs of the complexes were 26, 30, and 15 °C, respectively. Consistent with the low T_gs, the polymer complexes were

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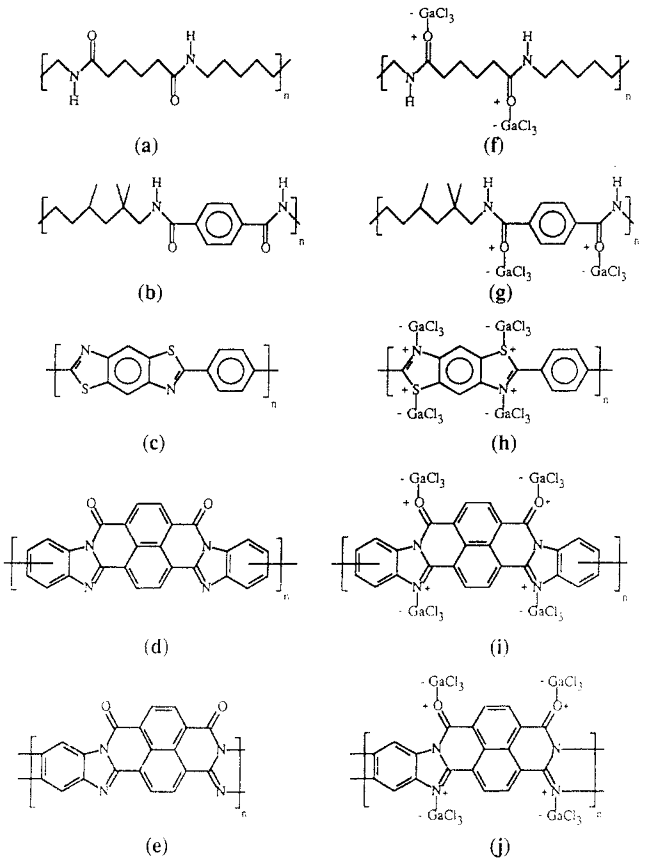

Figure 1. Molecular structures of the polymers investigated: nylon 66 (a), PTMHT (b), PBZT (c), BBB (d), BBL (e), $GaCl_3$–nylon 66 (f), $GaCl_3$-PTMHT (g), $GaCl_3$-PBZT (h), $GaCl_3$-BBB (i), and $GaCl_3$-BBL (j).

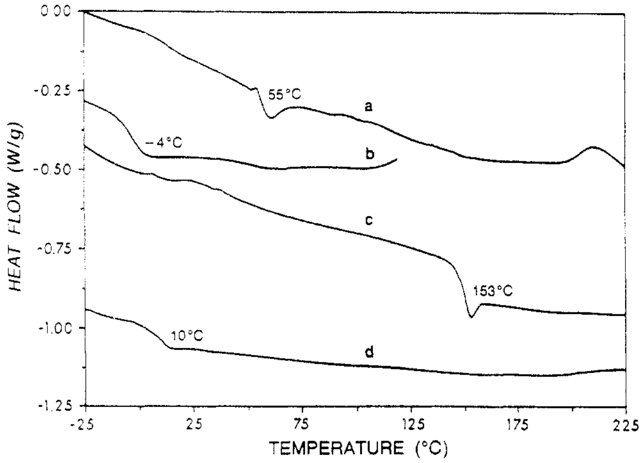

Figure 2. DSC thermograms obtained at a heating rate of 20 °C/min: nylon 66 (a), $GaCl_3$–nylon 66 (b), PTMHT (c), and $GaCl_3$-PTMHT (d).

rubbery and stretchable at 30 °C or higher. Figure 4 shows the temperature-dependent storage modulus (E') and loss tangent (tan δ) curves for the $GaCl_3$ complex of PBZT at a frequency of 0.16 Hz. The modulus scale of Figure 4 is relative since the sample was in between two glass plates. The loss tangent exhibited a minimum (T_δ) at 24 °C, which we take as the mechanical glass transition temperature and is very close to the calorimetric T_g measured by DSC. Similar experiments for the $GaCl_3$ complexes of BBB and BBL revealed T_δs of 12 and 29 °C, which are lower and higher, respectively, than the calorimetric T_gs. These glass transitions were reproducible on repeated thermal cycling up to 175 °C, above which the complexes start to decompose. These results show a shift in T_g to a lower temperature by 470–485 °C. This dramatic shift in T_g of high-temperature polymers on complexation can be explained in terms of the reduction in intermolecular forces, as with the polyamides. Theoretical calculations of the intermolecular interactions in the three polymers show them to be dominated by strong attractive van der Waals forces.[21,22] The net attractive intermolecular interaction energies between two chains packed face-to-face in a minimum energy arrangement in PBZT, BBB, and BBL have been estimated to be 123, 188.7, and 156.5 kJ/mol, respectively.[21,22] Since the van der Waals forces fall off as the inverse sixth power of interchain distance,[7,21,22] even small increases in interchain separation will produce very large decreases in the intermolecular forces. Clearly, complexation forces the chains apart and consequently reduces the intermolecular forces and increases the free volume.

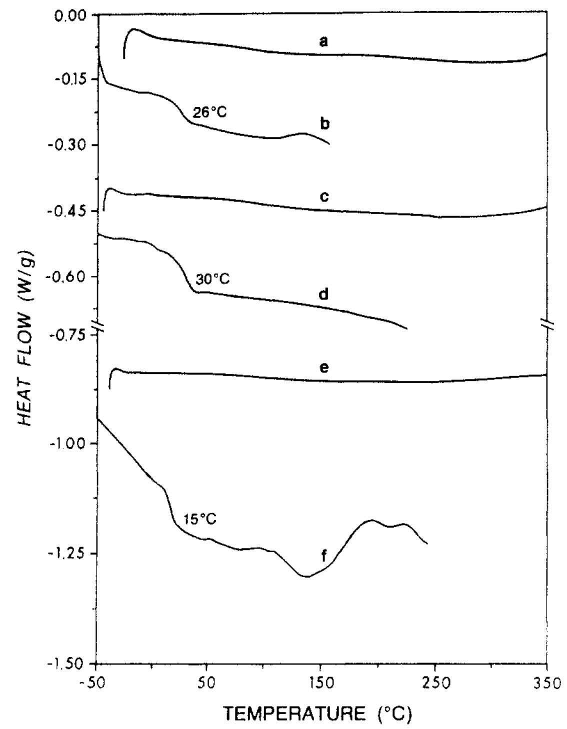

Figure 3. DSC thermograms obtained at a heating rate of 20 °C/min: PBZT (a), $GaCl_3$-PBZT (b), BBB (c), $GaCL_3$-BBB (d), BBL (e), and $GaCl_3$-BBL (f).

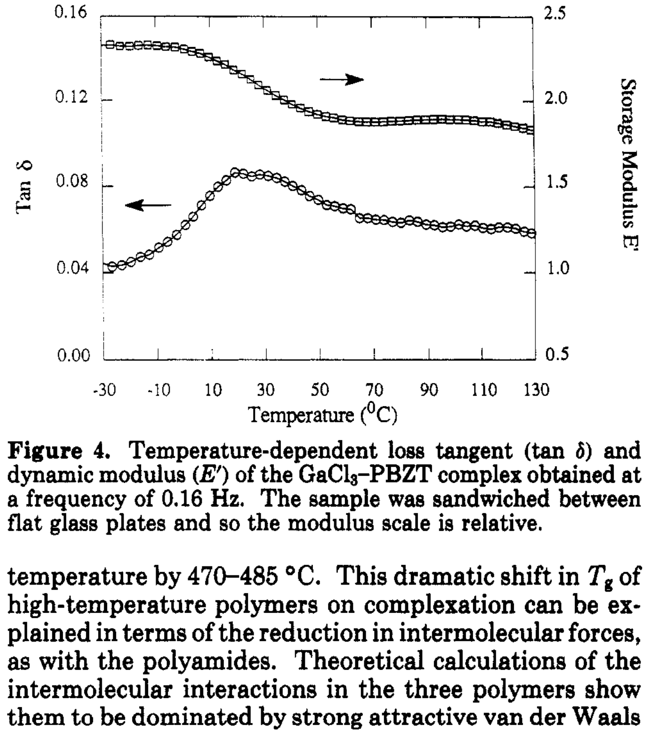

Figure 4. Temperature-dependent loss tangent (tan δ) and dynamic modulus (E') of the $GaCl_3$-PBZT complex obtained at a frequency of 0.16 Hz. The sample was sandwiched between flat glass plates and so the modulus scale is relative.

The very low and virtually same T_g values (15–30 °C) observed for the complexes of PBZT, BBB, and BBL warrant further comment. Light scattering studies[23-25] have shown that BBB is a semiflexible chain polymer that does not form mesophases, and BBL and PBZT have rodlike conformations that permit them to form lyotropic mesophases. Chain stiffness, rodlike conformation, and π-conjugation length of PBZT and BBL are retained in their complexes, as shown previously by their lyotropic mesophase formation[9,10] and UV-visible spectra. On the other hand, chain stiffness is an often cited molecular factor leading to a high T_g.[1-6] The present results demonstrate that intermolecular forces can have a dominant influence on the glass temperature of polymers.

One of the practical applications of reversible Lewis acid-base complexation of polymers is in developing novel processing techniques for polymers with diverse topologies and strong intermolecular interactions.[8-12] It has been shown that strong intermolecular forces (e.g., hydrogen bonding) represent the fundamental barrier to ultradrawing of flexible chain polymers, such as the polyamides, to high draw ratios and, consequently, high mechanical strength and stiffness using techniques such as tensile drawing or gel spinning.[26,27] Our approach provides a way to temporarily suppress the effects of strong intermolecular forces while processing, allowing large-scale deformation and fabrication to the desired form, and then to restore the forces to the finished oriented material where the interactions are needed for mechanical strength and stiffness. We note that the T_g and other physical properties of the polymers are recovered after decomplexation by treatment of the complexes with water or methanol.

A detailed investigation of the effects of intermolecular interactions on the T_g and other physical properties of polymers by Lewis acid coordination complexation is currently in progress, including computational modeling of the processes and structures and spectroscopic characterization of the solid complexes.[28]

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References and Notes

(1) Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1974; Vol. 1, p 18ff.

(2) Roe, R. J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley: New York, 1988; Vol. 7, pp 531-544.

(3) Lee, W. A.; Rutherford, R. A. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds., John Wiley: New York, 1975; p III-139.

(4) Mandelkern, L. *An Introduction to Macromolecules*, 2nd ed.; Springer-Verlag: New York, 1972.

(5) Billmeyer, F. W., Jr. *Textbook of Polymer Science*, 3rd ed.; John Wiley: New York, 1984.

(6) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.

(7) Rigby, M.; Smith, E. B.; Wakeman, W. A.; Maitland, G. C. *The Forces Between Molecules*; Clarendon Press: Oxford, 1986.

(8) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Polym. Mater. Sci. Eng.* **1989**, *60*, 404-409.

(9) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* **1989**, *22*, 3216-3222.

(10) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419-4429.

(11) Jenekhe, S. A. U.S. Patent 4,963,616, Oct 16, 1990.

(12) Jenekhe, S. A.; Peterson, J. R. U.S. Patent 4,945,156, July 31, 1990.

(13) Roberts, M. F.; Jenekhe, S. A. *Polym. Commun.* **1990**, *31*, 215-217.

(14) (a) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1990**, *2*, 224-226. (b) Roberts, M. F.; Jenekhe, S. A. *Mater. Res. Soc. Proc.* **1991**, *215*, 23-28.

(15) Roberts, M. F.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 3142-3146.

(16) Jensen, W. B. *The Lewis Acid-Base Concepts*; Wiley-Interscience: New York, 1980.

(17) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

(18) Allen, S. R.; Farris, R. J.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 2727-2734.

(19) Hergenrother, P. M.; Levine, H. H. *J. Polym. Sci., Part A-1* **1966**, *4*, 2341-2347.

(20) Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 451-478.

(21) Bhaumik, D.; Welsh, W. J.; Jaffé, H. H.; Mark, J. E. *Macromolecules* **1981**, *14*, 951-953.

(22) Nayak, K.; Mark, J. E. *Makromol. Chem.* **1986**, *187*, 1547-1550.

(23) Berry, G. C. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 143-172.

(24) Wong, C.-P.; Berry, G. C. *Polymer* **1979**, *20*, 229-240.

(25) Berry, G. C. *Polym. Mater. Sci. Eng.* **1985**, *52*, 82-83.

(26) Postema, A. R.; Smith, P.; English, A. D. *Polym. Commun.* **1990**, *31*, 444-447.

(27) Smook, J.; Vos, G. J. H.; Doppert, H. L. *J. Appl. Polym. Sci.* **1990**, *41*, 105-116.

(28) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.*, submitted.