(4) Morawetz, H. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 404-410.
(5) Frank, C. W.; Gashgari, M. A. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 387-403. Frank, C. W. *Plast. Compd.* **1981** (Jan-Feb), 67-74.
(6) Redpath, A. E. C.; Winnik, M. A. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 75-92. Svirskaya, P.; Danhelka, J.; Redpath, A. E. C.; Winnik, M. A. *Polymer*, in press. See also: Cuniberti, C.; Perico, A. *Eur. Polym. J.* **1980**, *16*, 887-893. Perico, A.; Cuniberti, C. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1435-1450.
(7) (a) Vincent, B.; Whittington, S. G. *Surf. Colloid Sci.* **1982**, *12*, 1-118. Fitch, R. M., Ed. "Polymer Colloids"; Plenum Press: New York, 1980. (b) Barrett, K. E. J., Ed. "Dispersion Polymerization in Organic Media"; Wiley-Interscience: London, 1975.
(8) (a) Vala, M. T., Jr.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886. (b) David, C.; Piens, M.; Gueskens, G. *Eur. Polym. J.* **1976**, *12*, 621-626. (c) Nakahira, T.; Maruyama, I.; Iwabuchi, S.; Kojima, K. *Makromol. Chem.* **1979**, *180*, 1853-1857. (d) Anderson, R. A.; Reid, R. F.; Soutar, I. *Eur. Polym. J.* **1979**, *15*, 925-929. (e) Phillips, D.; Roberts, A. J.; Soutar, I. *Polymer* **1981**, *22*, 427-429. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 411-421. (f) Sommersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218. (g) De Schryver, F. C.; Demeyer, K.; van der Auweraer, M.; Quanten, E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 93-108.
(9) For experiments describing energy transfer from naphthalene to anthracene in methacrylate copolymers containing both chromophores, see: Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 11-23.
(10) (a) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973. (b) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1971.
(11) This is the value taken from Berlman[10] for energy transfer from 1-methylnaphthalene to 1-methylnaphthalene.
(12) Göselle, U.; Hauser, M.; Klein, U. K. A.; Frey, R. *Chem. Phys. Lett.* **1975**, *34*, 519-522. Klein, U. K. A.; Frey, R.; Hauser, M.; Göselle, U. *Ibid.* **1976**, *41*, 139-142.
(13) Birks, J. B.; Georghiou, S. *J. Phys. B.*, (*Proc. Phys. Soc.*), *Ser. 2*, **1968**, *1*, 958-965.
(14) Veksli, Z.; Miller, W. G.; Thomas, E. L. *J. Polym. Sci. Polym. Symp.* **1976**, *No. 54*, 299-313.
(15) Young, D. M.; Crowell, A. D. "Physical Adsorption of Gases"; Butterworths: London, 1962.

Notes

Differential Scanning Calorimetry Characterization of Polypropylene. Dependence of T_g on Polymer Tacticity and Molecular Weight

DAVID R. BURFIELD*

Department of Chemistry, University of Malaya, Kuala Lumpur 22-11, Malaysia

YOSHIHARU DOI

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan.
Received May 7, 1982

Whereas the dependence of the glass transition temperature (T_g) on polymer tacticity has been well defined for certain polymers, notably the poly(alkyl methacrylates), the situation for polypropylene (PP) is still ambiguous.[1,2] This may in part stem from a failure to study polymer samples that have been carefully characterized with respect to both molecular weight and tacticity and in part to lack of consistency in T_g measurements.

Molecular weight determination is crucial since earlier work[3] has shown that the T_g value for atactic PPs falls dramatically in the low molecular weight region ($M_n <$ 50000). Furthermore, as illustrated below, the steric purity of PPs is rarely complete, being determined by catalyst type as well as reaction conditions. Consequently, an absolute method[4] for tacticity determination such as ^{13}C NMR must be considered mandatory for establishment of the stereochemical configuration.

We now report T_g values derived from standardized DSC measurements for well-characterized PP samples of varying tacticity.

Experimental Section

Polypropylene samples of varying stereoregularity and molecular weight were prepared with titanium and vanadium catalyst systems as follows: samples 1-4, $TiCl_4/C_6H_5COOC_2H_5/MgCl_2-Al(C_2H_5)_3$ system at 314 K; sample 5, $TiCl_4/C_6H_5COOC_2H_5/MgCl_2-NaAl(C_2H_5)_4$ system at 314 K; samples 6-8, $V(acac)_3-Al(C_2H_5)_2Cl$ system at 195 K; sample 9, $V(acac)_3-Al(C_2H_5)Cl_2$ system at 195 K; sample 10, $V(acac)_3-Al_2(C_2H_5)_3Cl_3$ system at 195 K; sample 11, $Ti(OC_4H_9)_4-Al(C_2H_5)Cl_2$ system at 313 K, sample 12, $Ti(OC_4H_9)_4-Al(C_2H_5)_2Cl$ system at 294 K; sample 13, $VCl_4-Al(C_2H_5)_2Cl$ system at 195 K; sample 14, $VCl_4-Al(C_2H_5)_3$ system at 195 K. Details of the polymerization procedure and purification of the polymers were previously described.[5-7] The stereoregularities of the samples were determined by ^{13}C NMR measurements using JEOL FX-200 and JEOL JNM PS-100 spectrometers on 15-30% (w/v) dichlorobenzene solutions at 413 K as detailed elsewhere.[5-7] The molecular weights of the samples were measured by GPC (Water Associates, Model 200) using five polystyrene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3-Å pore sizes) and *o*-dichlorobenzene as solvent at 408 K.

DSC measurements were made with a Perkin-Elmer Model DSC-2C instrument equipped with a liquid nitrogen subambient accessory. In order to ensure good reproducibility, the liquid nitrogen reservoir was filled 2 h before calibration and maintained approximately three-fourths full throughout measurement. The temperature scale was calibrated against mercury (234.28 K), water (273.15 K), and indium (429.78 K) at a scan rate of 10 K/min.

Polymer samples (ca. 5 mg) were encapsulated in aluminum pans. Samples were pretreated at 473 K for 5 min, quenched (320 K/min) to about 60 K below T_g, and scanned through T_g at 10 K/min. Highly isotactic samples were found to crystallize under these quench conditions and consequently they were heated at 473 K outside the instrument, were quenched by dropping directly into liquid nitrogen, and were then inserted into the DSC sample holder below T_g and scanned as above.

Values of T_g were calculated with the Perkin-Elmer standard TADS program. The reproducibility of duplicate runs of samples with well-defined T_g was better than ±0.2 K.

Results and Discussion

The thermograms of samples representative of atactic, syndiotactic, and isotactic PP are displayed in Figure 1. The glass transition temperatures of the atactic and syndiotactic samples were found to be well defined whereas invariably the magnitude of the base line shift associated with the glass transition was much smaller for the isotactic samples and furthermore the transition was partially obscured by the onset of crystallization. It seems probable that the highly isotactic samples were not completely amorphous despite quenching directly into liquid nitrogen. The rapidity of crystallization for the highly isotactic PP samples is illustrated by Figure 2, which shows the onset of crystallization at 395 K despite quench cooling at 320 K/min. During the course of the heating scan the pre-

0024-9297/83/2216-0702$01.50/0

Table I
DSC Analysis of Polypropylenes

sample no.	stereoregularity (steric triad fraction) [mm]	[mr]	[rr]	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	T_g,[a] K	T_g,[b] K
				Syndiotactic			
9	0.04	0.28	0.68	10 600	1.6	264.6	266.1
6	0.03	0.33	0.64	14 800	1.1	265.3	266.9
7	0.03	0.30	0.67	32 800	1.2	267.2	269.0
8	0.03	0.32	0.65	37 500	1.1	267.9	269.2
13	0.00	0.24	0.76	35 800	1.7	267.2	269.0
10	0.03	0.28	0.69	86 900	1.9	268.5	269.9
				Atactic			
11	0.35	0.37	0.28	3 800	1.8	249.2	250.8
12	0.49	0.31	0.20	3 700	1.9	250.2	252.7
1	0.43	0.30	0.27	12 000	5.1	263.1	264.7
14	0.28	0.39	0.33	754 000	3.3	266.2	268.2
				Isotactic			
2	0.78	0.13	0.09	18 000	3.3	255.9[c]	
3	0.93	0.05	0.02	45 000	5.3	254.5[c]	
4	0.94	0.04	0.02	75 000	4.8	255[c,d]	
5	0.99	0.01	0.00	413 000	5.2	259[c,d]	

[a] T_g onset measured at 10 K/min after quenching (320 K/min) from 473 K. [b] T_g midpoint value. [c] Samples quenched directly with liquid nitrogen and introduced into DSC cell at 200 K. [d] Glass transition indistinct; T_g values determined at 80 K/min.

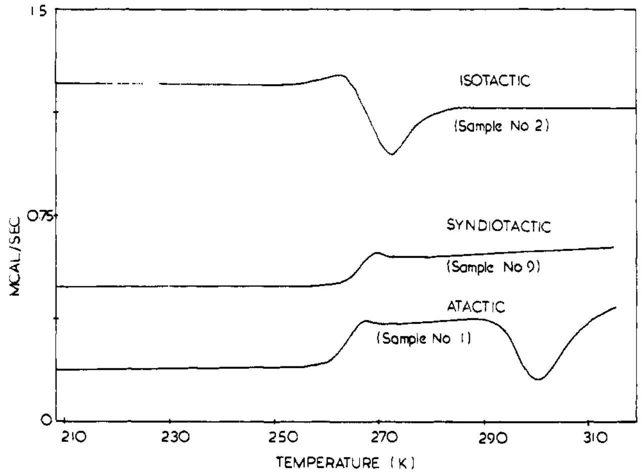

Figure 1. DSC thermograms of PP samples of varying tacticity in the T_g region. (Scan rate 10 K/min.)

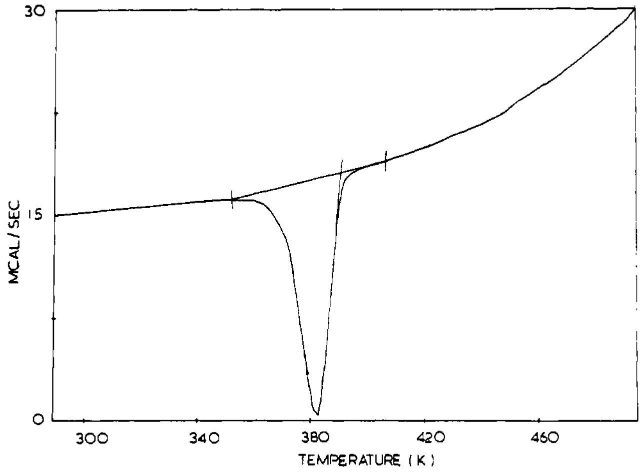

Figure 2. Crystallization during quench cooling of isotactic polypropylene.

dominantly atactic samples also show a tendency to crystallize,[9] albeit to a much lower extent than the isotactic samples and some 30 K above the T_g. The syndiotactic samples show no such tendency.

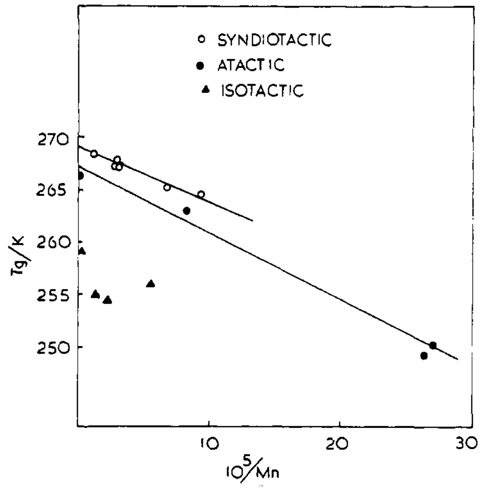

Figure 3. Dependence of T_g on the reciprocal of $\bar{M}_n$ for PP samples of varying tacticity.

Table II
Summary of Limiting T_g Values at High Molecular Weight

tacticity	T_g, K
syndiotactic	269.2 ± 0.2
atactic	267 ± 1
isotactic	255 ± 2

The values of T_g for the various PP samples examined are summarized in Table I. On average, at a heating rate of 10 K/min the midpoint of the glass transition is approximately 1.6 K higher than the onset value for the atactic and syndiotactic samples. The midpoint value for the isotactic samples could not be accurately determined because of concomitant crystallization.

Consistent with earlier studies[2,3] the number-average molecular weight $\bar{M}_n$ of the polymer is seen to have a pronounced influence on T_g. The data show a reasonable correlation between T_g and the reciprocal of $\bar{M}_n$ (Figure 3) except for the isotactic samples, where the precision of T_g measurement was reduced because of the factors already discussed.

On comparison of the limiting values of T_g at high molecular weight (Table II) a clear dependence upon tacticity may be discerned. The T_g decreases in the series $T_{g_{syndio}} > T_{g_{atactic}} \gg T_{g_{isotactic}}$. This exactly parallels the trend observed with poly(methyl methacrylate),[1,10] where again the isotactic configuration is characterized by a significantly lower T_g. The results are in contrast with earlier predictions[11] that monosubstituted polymers such as polypropylene should show no significant dependence of T_g stereoregularity. The difference in glass transition temperature (ΔT_g) between the syndiotactic and isotactic forms of polypropylene of ~14 K is, however, much smaller than that for poly(methyl methacrylate),[10] $\Delta T_g \sim$ 81 K.

These results also cross correlate with the recent observation[8] that ^{13}C NMR spin–lattice relaxation times, T_1's, are considerably longer for isotactic than for syndiotactic PP sequences. Taken together, these findings appear to indicate a greater freedom in the segmental motion of the isotactic polymers.

The T_g value reported here for atactic polypropylene (267 ± 1 K) is close to the value recorded earlier[2,3] by DSC measurements for high molecular weight atactic polypropylene (266 K), but the isotactic T_g value (255 ± 2 K) is at variance with the earlier[2] value of 272 K. The discrepancy may be due to inadequate characterization or quenching of the PP samples in the earlier work, since the presence of crystallinity tends to increase the T_g of the sample.

Registry No. Syndiotactic polypropylene, 26063-22-9; atactic polypropylene, 9003-07-0; isotactic polypropylene, 25085-53-4.

References and Notes

(1) See, for example, T_g values summarized in: Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley-Interscience: New York, 1975.
(2) Cowie, J. M. G. *Eur. Polym. J.* **1973**, *9*, 1041.
(3) Ke, B. *J. Polym. Sci., Part B* **1963**, *1*, 167.
(4) Solvent extraction or IR measurement cannot be regarded as a reliable standard for tacticity determination since these methods are dependent on the molecular weight and crystallinity of the polymer samples.
(5) Doi, Y. *Macromolecules* **1979**, *12*, 1012.
(6) Doi, Y.; Suzuki, E.; Keii, T. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 293.
(7) Doi, Y.; Nishimura, Y.; Keii, T. *Polymer* **1981**, *22*, 469.
(8) Asakura, T.; Doi, Y. *Macromolecules* **1981**, *14*, 72.
(9) This reproducible effect may be indicative of some short stereoblock units in these otherwise predominantly atactic samples.
(10) Biros, J.; Larina, T.; Trekoval, J.; Pouchly, J. *Colloid Polym. Sci.* **1982**, *260*, 27.
(11) Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1968**, *1*, 537.

Communications to the Editor

Soluble Polyacetylene Graft Copolymers[†]

Polyacetylene, a semiconducting organic polymer, undergoes dramatic changes in conductivity upon appropriate doping. Inspired by the expectation of producing a commercially viable conducting plastic, various workers have devoted extensive study to this polymer for more than 2 decades.[1] Among known conductive polymers, polyacetylene exhibits the potentially most useful electrical and electronic properties; however, all previously reported forms of the material have undersirable physical properties such as complete insolubility and decomposition without melting.[2]

Recent experimental work has focused primarily on silvery, free-standing films prepared by polymerizing gaseous acetylene on a layer of concentrated Ziegler–Natta catalyst solution, as reported by Shirakawa in 1971.[3,4] While macroscopically homogeneous, such films are microscopically inhomogeneous, consisting of a tangled mat of fibers approximately 15 nm in diameter, in which polymer chains reportedly orient along the fiber axis.[5–7] Film densities are typically ~0.4 g/cm^3.[8,9]

Understanding the fundamental electronic properties of polyacetylene necessitates the separation of intramolecular, or single chain, effects from those induced by intermolecular, or chain–chain interactions. Attempts to solve this problem, usually by modifying the monomer, have in all cases resulted in materials with inferior electrical properties.[10–12] We have prepared a new type of polyacetylene which is soluble in various common organic solvents by incorporating the polyacetylene into a graft copolymer.

It has been known for over 2 decades that block and graft copolymers exhibit unique properties, unlike those of homopolymer blends. In particular, these systems exhibit significantly altered phase diagrams, characterized by an elevated critical point[13] and phase morphologies that are restricted in size to molecular dimensions.[15,16] With this in mind, we have prepared several copolymers containing a single block of polyacetylene grafted to various carrier polymers in an effort to exploit the solubility that results from block or graft copolymerization.[17] Two such graft copolymers are discussed in this communication, one prepared with polyisoprene (80% cis 1,4, 15% trans 1,4, 15% 3,4) at −78 °C and the second with polystyrene at 25 °C, denoted PI_{200}–PA and PS_{200}–PA, respectively. Both the polyisoprene and polystyrene carrier polymers are nearly monodisperse with a molecular weight of 2×10^5 and have been modified through oxidation to contain electrophilic sites.

The graft copolymers were synthesized by polymerizing acetylene with a $Ti(OC_4H_9)_4/Al(C_2H_5)_3$ catalyst[3] in a toluene solution containing the carrier polymer. Intensely maroon or blue solutions were formed, characteristic of the cis and trans isomers of polyacetylene, respectively. These solutions are stable but sensitive to degradation by oxygen. We believe the grafting step to be the result of nucleophilic attack of the growing polyacetylene chains on electrophilic sites on the carrier polymer, which also terminates polyacetylene chain growth. These sites can be introduced onto polyisoprene with molecular oxygen to give aldehydes and ketones or, more selectively, with *m*-chloroperbenzoic acid, which introduces epoxides without chain scission. Unoxidized polyisoprene is ineffective as a carrier polymer. During the polymerization of the polystyrene carrier chains a small proportion of butadiene was introduced to provide sites for subsequent oxidation or epoxidation. The epoxidized styrene–butadiene copolymer is particularly useful for morphological work since polyacetylene can be selectively stained with osmium tetraoxide.[16]

The molecular weight of the polyacetylene units was estimated by infrared analysis on samples that had been

---

[†] Presented in part at the International Conference on Low Dimensional Conductors, Les Arcs, France, Dec 11, 1982.