Nanoblends of Incompatible Polymers by Direct Space-Confined Polymerization

Shu-Hua Chan, Yi-Yang Lin, and Ching Ting*

Union Chemical Laboratories, Industrial Technology
Research Institute, 321 Kuang-Fu Road, Sec. 2,
Hsinchu 300, Taiwan, ROC

Received August 10, 2003
Revised Manuscript Received October 11, 2003

Polymer synthesis in a controlled fashion in regard to the microstructure as well as morphology is of fundamental interest and practical importance. Recent developments in organometallic catalysts allow polymers with more precise control of microstructure, molecular weight, and molecular weight distribution to be made.[1,2] However, the polymer morphology can still only be manipulated by processing. Recent investigations aimed at using mesoporous silicates with uniform pore size and regular orientation such as MCM-41[3,4] as supported materials in polymerization reaction have demonstrated the feasibility of controlling morphology along with microstructure of the polymer during the reaction.[5−8] However, to our best knowledge, loading two catalytic systems within the pores of this oriented solid support to make two polymers simultaneously has never been demonstrated. The significance of this development is the ability to blend two polymers to nanoscale range through direct reaction without the need of a compatibilizer. The importance of this becomes more pronounced when certain end use requirements are to be met.

In polymer processing, a second polymer is normally added to the main one by a blending technique either by conventional physical blending[9,10] or a reactor blending technique.[11] However, the limits of the above techniques are in the micrometer scale range. Nonstop efforts, thus, have been made in both cases to avoid phase separation including adding various types of compatibilizer. Reactor blends in theory would perform better than physical blends as far as the homogeneity issue is concerned due to blending during polymer formation. Unfortunately, two catalysts within one reactor often suppresses one catalyst's activity over that of the other, possibly owing to catalyst interaction or competition reactions.

This study presents a novel method of preparing two polymers with nanoscaled blending through space-confined polymerization. Suitable catalysts/initiators are sequentially supported onto surface of mesoporous silicate such as MCM-41. This dual catalytic system is then exposed to two monomers simultaneously to generate polymer blends. Ethylene homopolymer is made from a catalyst prepared by pretreating the mesoporous support with the cocatalyst, methylaluminoxane (MAO), prior to adding the metallocene precursor, zirconocene dichloride (Cp_2ZrCl_2 where Cp stands for the cyclopentadienyl ligand). When a tubules-within-tubule type of MCM-41[12] is used, the initial stage of PE formation can be directly observed by SEM (Figure 1). Syndiotactic polystyrene (sPS) is polymerized by pentamethylcyclopentadienyl titanium trimethoxide ($Cp^*Ti(OMe)_3$ where Cp* is pentamethylcyclopentadienyl ligand)[13] and MAO supported on mesoporous silicate. Atactic polystyrene (aPS) is polymerized by a free radical initiator, azobis(isobutyronitrile) (AIBN), also supported on mesoporous silicate. The resulting polymer are collected as methanol-insoluble part. In these reactions, the activity is so high that the inorganic residue is in the range of ppm level. When any of the two polymers from above are made simultaneously, two corresponding catalyst precursors are supported onto the mesopore respectively and the mesoporous support used in the nanoblending reactions is SBA-15 with a pore size of about 6.0 nm.[14]

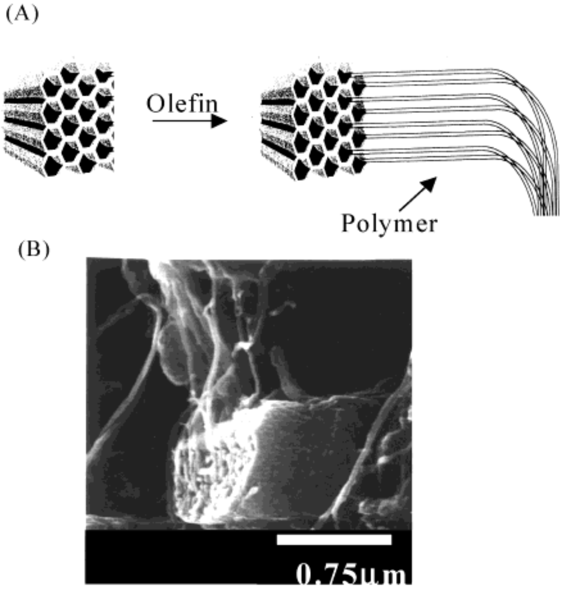

Figure 1. (A) Structure of the polymer made from catalyst supported on mesoporous material and (B) SEM of PE produced by Cp_2ZrCl_2 supported on crystalline TWT-MCM-41.

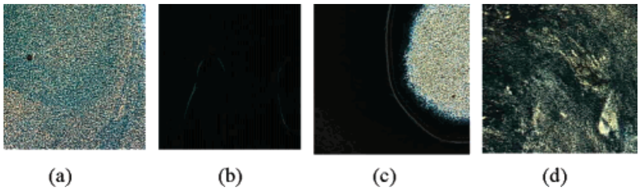

Figure 2. Microscopic contrast of sPS and aPS blends with and without mesoporous support. Birefringence pattern of (a) sPS, (b) aPS, and (c) sPS and aPS reactor blends without mesoporous support and (d) sPS and aPS blend from mesoporous supported system.

When aPS and sPS polymer blends are made by this method, a polarizing optical microscope (POM) with cross-polarized light showed an evenly blended two polymers in contrast to the reactor blend of two polymers by two unsupported catalysts in one reactor (Figure 2). Even the reactor blend method under normal reaction conditions does not solve problems such as phase separation while our approach demonstrates a much more satisfactory outcome. As is well-known, aPS is soluble in methyl ethyl ketone (MEK) even at room temperature. Solvent extraction is performed on pure aPS and aPS/sPS from space-confined polymerization while techniques such as physical aging by DSC[15,16] are used to monitor the amount of amorphous phase re-

---

* Corresponding author. E-mail: cting@itri.org.tw.

10.1021/ma035174q CCC: $25.00

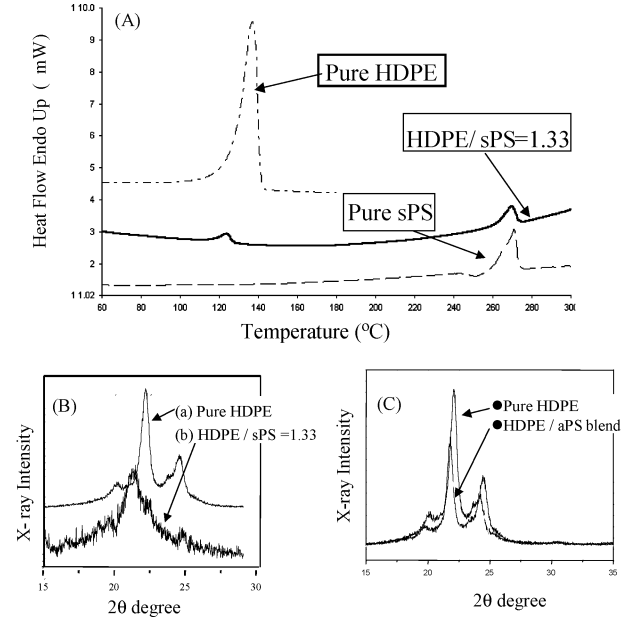

Figure 3. (A) Comparison of DSC scans of nanoblended HDPE and sPS with PE/sPS mole ratio = 1.33 (by ^{13}C NMR) with unblended samples. (B) Crystallinity of (a) HDPE and (b) nanoblended PE with sPS with PE/sPS mole ratio = 1.33 by XRD. (C) XRD of nanoblended PE with aPS.

maining from the MEK extraction experiment for a aPS/sPS blends sample. According to our results, significant amounts of aPS still remained even after 72 h of MEK extractions while no aPS remained from the reactor blend sample after 1 h extraction under the same condition. This finding strongly suggests that aPS and sPS polymer chains are highly dispersed and entangled so that spatial confinement imposed on aPS may prohibit its removal by solvent extraction.

PE and PS nanoblends demonstrate more significance in blending effectiveness of two incompatible polymers when using this technology. When PE and sPS are made simultaneously by dual catalysts within mesoporous channels, the crystallinity of PE is suppressed dramatically by both DSC and XRD (Figure 3, parts A and B) while the physical blends usually merely show crystallinity reduction in proportion.

The crystallinity of PE decreased by a significant amount (ΔH of DSC for PE at 123 °C decreases from 190 to 10.38 J/g) despite the fact that the mole ratio of sPS/PE in this sample is only 3/4 by NMR. Meanwhile, the crystallinity of sPS in the same sample is reduced less significantly (ΔH decreases from 32 J/g for pure sPS to 11 J/g in this blend). As the ^{13}C NMR spectrum of this sample rules out the possibility of copolymer formation, the crystallinity suppression of PE can only be attributed to the lack of homogeneous nucleation due to the existing sPS crystal structures while cooling. This crystallinity observation is owing to the existence of two crystalline polymers with different crystallization temperature (T_c) and crystallization rate. The sPS spherulites being at higher T_m and T_c would present during PE's melting and crystallizing. The evenly distributed sPS domains would hinder the PE spherulite growth, thus lowering the heat of crystallization (ΔH) for PE; meanwhile, the reverse situation is not as serious.

When PE is co-formed with aPS, the degree of crystallinity reduction is not as obvious (Figure 3C) since the latter lacks crystallinity despite the fact that the degree of dispersion of both sPS and aPS among the PE matrix is amazingly even as shown by TEM (Figure 4) with the domain size ranging from 150 nm for sPS to an even smaller (about 50 nm) size for aPS in the PE matrix, respectively. We believe that this phenomenon occurs because when two polymers are formed from dual catalysts in a space-confined manner, chain entanglements are forced to occur. However, since two catalytic sites have different chain termination rates, a polymer with a longer chain (i.e., PE) will behave as a matrix while the shorter chain ones will be evenly dispersed within.

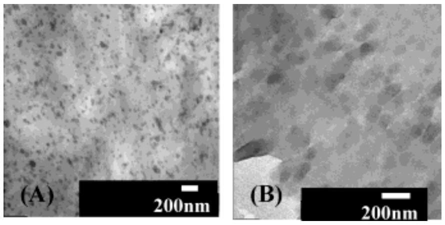

Figure 4. TEM images of nanoblended (A) PE/aPS and (B) PE/sPS. The dark phases are the PS phase stained with diluted RuO$_4$ solution for 17 min.

In conclusion, this study demonstrates that space-confined polymerization of two monomers by dual catalytic sites is an effective approach to synthesize polymer blends with nanoscaled dispersion. The duel catalysts in this novel polymerization method offer independent active sites during the polymerization so as to generate the ultimate blends of the two polymers. The even dispersion of one polymer over the other may be due to combination effect of high activity of the catalysts and different chain termination rate for two processes. The unique feature of the resulting polymer blends and straightforward reaction control make this approach more attractive to make a polymer blend.

We have only shown information key to this study in this brief communication. It will be shown in a future paper that this polymerization method is novel to produce a wide range of polymer blends. We have also observed that annealing of sPS/PE blends at 300 °C for 1 h has basically no effect on ΔH's for either PE or sPS domains. The reason for this, however, is still under investigation in this laboratory.

Acknowledgment. We acknowledge Ministry of Economic Affairs, Taiwan, for generous financial support. We thank greatly Professor C.-Y. Mou and Dr. H.-P. Lin at National Taiwan University for providing mesoporous materials and XRD analysis.

Supporting Information Available: Text giving detailed experimental information for catalyst preparation and a table of polymerization results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143.
(2) Helmut, G.; Koppl, A. *Chem. Rev.* **2000**, *100*, 1205.
(3) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
(4) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olsen, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
(5) Kageyama, K.; Tamazawa, J.; Aida, T. *Science* **1999**, *285*, 2113.
(6) Tajima, K.; Aida, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4821.

(7) Ng, S. M.; Ogino, S.; Aida, T. *Macromol. Rpaid Commun.* **1997**, *18*, 991.
(8) Lehmus, P.; Rieger, B. *Science* **1999**, *285*, 2081.
(9) Abis, L.; Abbondanza, L.; Graglia, R.; Castellani, L.; Giannotta, G.; Po, R. *Macromol. Chem. Phys.* **2000**, *201*, No 14, 1732.
(10) Li, J.; Shanks, R. A.; Long, Y. *J. Appl. Polym. Sci.* **2003**, *87*, 1179.
(11) Mecking, S. *Macromol. Rapid Commun.* **1999**, *20*, 139.
(12) Lin, H.-P.; Mou, C.-Y. *Science* **1996**, *273*, 765.
(13) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.
(14) Lukens, W. W.; Schmidt-Winkel, P., Jr.; Zhao, D.; Feng, J.; Stucky, G. D. *Langmuir* **1999**, *5403*, 3.
(15) Hong, B. K.; Jo, W. H.; Kim, J. *Polymer* **1998**, *39*, No. 16, 3753.
(16) Zhao, J.; Fan, O. *Polym. Bull. (Berlin)* **2001**, *47*, 91.

MA035174Q