Perspective

PCHE-Based Pentablock Copolymers: Evolution of a New Plastic

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Introduction

Plastics are everywhere, hardly a revelation to a chemical engineer. After nearly a century of development, synthetic polymers continue to grow in importance, accounting for \$304 billion in shipments in the U.S. in 1999 (The Society of Plastics Industry, 2001). A major share of this market—roughly 70%—is accounted for by just four commodity plastics: polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinylchloride (PVC). Yet, these few inexpensive compounds cannot satisfy all the combinations of physical property requirements associated with the plethora of new and existing applications; these include high modulus, toughness, elasticity, clarity, surface texture, elevated use temperature, chemical resistance, impermeability to gases, electrical resistance, environmental stability, low density, and ease of processing. A commonly accepted adage holds that the discovery of new commodity monomers is virtually impossible. This article outlines an alternative approach, modification of an existing commodity plastic—polystyrene—in order to satisfy the growing optical media market. Development of this new class of materials was made possible by a unique, interactive, and interdisciplinary partnership between industry and academia.

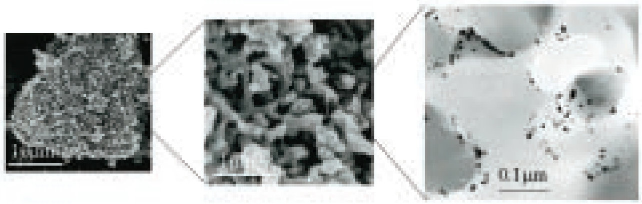


Figure 1. Transmission electron microscopy (TEM) (right) and scanning electron microscopy (SEM) (left and center) images of the Pt/SiO$_2$ hydrogenation catalyst developed by Dow for saturation of polystyrene. Increasing levels of magnification reveal a coral-like silica substrate with sub-micron size pores that supports small (ca. 10 nm dia.) platinum particles.

Optical media such as CD and DVD (recordable and random access) have grown over the past decade into the preferred form of storing and retrieving electronically generated information. As data density increases, the size of the features required for optical media decreases, placing ever increasing demands on the engineering properties and processibility of the plastic substrates. Polycarbonate, the material currently used for most optical applications, absorbs light at the frequencies proposed for the next generation of storage devices. In order to be competitive, an alternative plastic must combine intrinsic clarity with a host of additional physical attributes including suitable toughness and melt processing characteristics, and, of course, low cost.

Development of PCHE

One candidate for these applications is hydrogenated polystyrene, also known as polycyclohexylethylene (PCHE). First made in 1929, synthesis of PCHE has been attempted by many groups. However, poor catalysts generally led to chain degradation and poor properties. Patents related to materials by Borg-Warner (Hoeg et al., 1971) and optical substrates by Mitsubishi (Murayama and Kasahara, 1990) generated some promise of new applications including in optical media, but these were not practiced commercially.

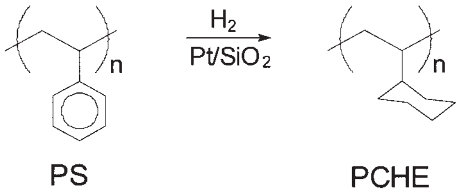
Modern interest in modifying the properties of unsaturated polymers, primarily polybutadiene and polyisoprene, was stimulated by an influential publication by Graessley and coworkers (Rachapudy et al., 1979). Recognizing the benefits of eliminating the sources of thermal and oxidative degradation during rheological characterization, these researchers exploited and compared the efficiency of various homogeneous and heterogeneous transition metal hydrogenation catalysts to saturate polybutadiene. More than a decade later, Gehlsen et al. (1995) discovered that palladium, dispersed on barium sulfate, could completely hydrogenate polystyrene and substituted styrenes (e.g., polyvinyl toluenes and poly *t*-butyl styrene), and polystyrene based block copolymers (Gehlsen and Bates, 1993) without chain degradation. Unfortunately, uneconomical amounts of catalyst were required to achieve these results. Yet, contrary to popular belief (Gergen et al., 1996), these block copolymers microphase separated at modest molecular weights. In fact molten PCHE and polyethylene (PE) (produced by saturating *1,4*-polybutadiene (*1,4*PB)) are less compatible thermodynamically than the PS and *1,4*-PB precursors (Gehlsen and Bates, 1994). Thus, saturated hydrocarbon block copolymers containing PCHE became promising candidates for commercial development (Gehlsen et al., 1994). Model synthesis (anionic polymerization and catalytic hydrogenation) combined with small-angle neutron and x-ray scattering (SANS and SAXS), and dynamic mechanical spectroscopy, established the fundamental structure-property relationships for this category of block copolymers (Gehlsen and Bates, 1993, 1994; Gehlsen et al., 1995).

Table 1. Physical Properties of Polystyrene (PS) and Polycyclohexylethylene (PCHE)

Property	PCHE	PS
Tg, °C	ca. 147	ca. 106
Density, g/cc	0.947	1.06
Heat Capacity, 25°C J/(gK°)	2.0	1.2
Dielectric Constant 1 kHz	2.26	2.53
Refractive Index Na d line (589 nm)	1.506	1.59
Total Transmittance	91%	91%
% Water Absorption, 23°C, 24 h	0.025	0.06
Coefficient of thermal expansion, $<T_g$ (µm/m·°C)	64	69
Poisson's Ratio	0.343*	0.337*
Flexural Modulus, GPa 25°C	2.8	3.1
M_e, Entanglement Mol. Wt.	40,000	13,309**
Stress-Optical Coefficient (Brewsters, 10^{-12} Pa^{-1})	-200	-4,700

*Measured by ultrasonic analysis at 5 MHz.
**Fetters et al. (1994).

Work begun independently at The Dow Chemical Company, which focused on using hydrogenation to increase the glass transition temperature (T_g) of PS, also showed that PCHE exhibited improved thermal, oxidative, and UV stability. Initial efforts at Dow were directed at saturating the diene portion of styrene-butadiene (SB) block copolymers using palladium dispersed on various mesoporous supports (Hucul, 1991, 1992). Further development of these novel heterogeneous catalysts with platinum as the active metal allowed for unusually high degrees of PS hydrogenation, previously considered an undesirable side reaction. A breakthrough was realized when this catalyst was employed with PS homopolymer (see Figure 1).



Profound increases in the rate of PS hydrogenation, run at higher concentrations and without degradation, were obtained (Hucul and Hahn, 2000). Instead of requiring 24 h with incomplete conversion, complete saturation could be effected in 60 to 90 min.

A new optical material

With an ample supply of material, and good prospects for large-scale production, Dow scientists began exploring the prospects for applying PCHE to optical media. Hydrogenation of PS leads to a litany of property changes, as summarized in Table 1. Most significantly, the glass transition temperature increases to about 147°C, while the density decreases 12%, with diminished water adsorption and a twenty-four fold reduction in the stress optical coefficient. These all represent significant and desirable improvements. Obviously, increasing T_g is an attractive feature for many applications. Since polymers for optical media are sold by weight, but used by volume, the density reduction offsets a portion of the cost of hydrogenation. The stress optical coefficient controls the birefringence associated with polymer chain orientation trapped during processing. PCHE exhibits a remarkably low value, ideal for molding clear DVDs.

Despite all these advantages, PCHE has one serious liability: The PCHE homopolymer is a brittle macromolecular glass. The origins of this deleterious property can be traced to the bulky pendant cyclohexyl group, which forces the chains into tight packing configurations, as quantified by small-angle neutron scattering (Gehlsen et al., 1995). Consequently, the entanglement molecular weight (M_e) increases to about three times that of PS (Fetters et al., 1994) (see Table 1). In order to achieve acceptable levels of toughness (e.g., some degree of ductility), a glassy polymer must have a molecular weight more than ten times M_e. Unfortunately, this complicates processing PCHE into the dimpled disks that are the basis for the CD and DVD industry. Replicating the master patterns with acceptable cycle times is virtually impossible at such elevated molecular weights due to high viscosity and melt elasticity.

Pentablock copolymers

Incorporation of PCHE into block copolymers represented a change in strategy at Dow. Nanoscale separation of rubbery polybutadiene or polyisoprene blocks is well known to impart toughness to glassy polymers such as PS, even at reduced molecular weights (Hsieh and Quirk, 1996). Original attempts with a classical CEC triblock architecture showed good processability and unexpected toughness. (In our block copolymer notation, C and E are shorthand for PCHE and PE, respectively.) Moreover, combining relatively stiff semicrystalline PE (approximately, 40% crystallinity) with glassy PCHE results in a superior elastic modulus, relative to the precursor SBS, while simultaneously eliminating light scattering. Fortuitously, PCHE (refractive index $n=1.506$) is nearly index matched with semicrystalline PE ($n \approx 1.51$), in contrast with PS ($n=1.59$) and *1,4*PB ($n=1.515$) (Brandrup and Immergut, 1989). This combination of refractive index matching and nanoscale structure results in exceptional optical clarity. Unfortunately, the overall balance of properties was not adequate to penetrate the optical media market. In early 1997, we all wondered, “How could this attractive material be further improved without sacrificing the desirable characteristics?”

A possible solution emerged during a discussion between project members, “Why not couple the CEC triblocks into CECEC pentablocks?” A single covalent bond would tie up all PCHE center blocks in bridging or entangled looping configurations, thereby covalently stitching every glassy domain into the semicrystalline PE ones (see Figure 2). This is straightforward to accomplish in practice. Either a five step sequential addition of styrene and butadiene monomers, or the use of a bifunctional coupling agent after anionic polymerization of three blocks, results in the pentablock architecture. Subsequent catalytic hydrogenation with the Dow catalyst leads to the desired product. Preliminary experiments at the University of Minnesota validated the pentablock hypothesis, yielding surprising improvements in tensile properties over analogous triblocks.

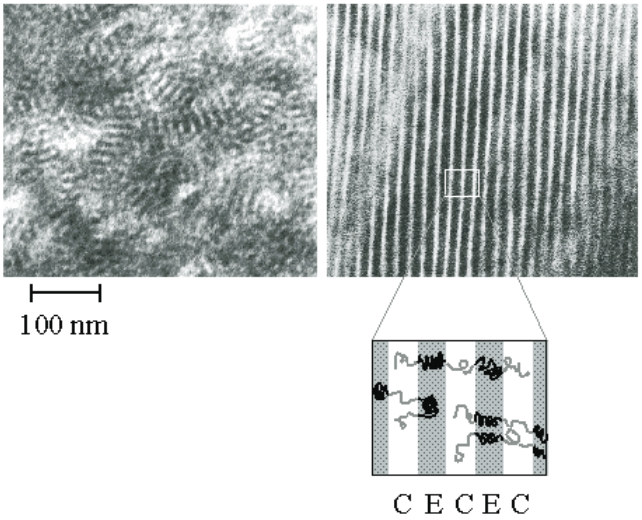


Figure 2. TEM images obtained from thin slices of the CECEC pentablock copolymer after staining with RuO_4. Cooling the melt below the order-disorder transition temperature (T_{ODT}) leads to nanophase separation, but only short-ranged order (left). Application of reciprocating shear spontaneously aligns the lamellae (right). The cartoon illustrates how the pentablock copolymer is distributed within the lamellae, with the center C block assuming bridging and looping conformations. On average, half the blocks within the C domains, and all the E blocks, are mechanically coupled through bridging and looping. These restrictions are speculated to inhibit coarsening of the morphology shown in the left panel and are associated with enhanced mechanical toughness. Also, the nanoscale structure, combined with nearly index matched semicrystalline E and glassy C domains, results in outstanding optical properties.

The overall molecular weight of the CECEC pentablock copolymer must be adjusted so as to place the order-disorder transition temperature (T_{ODT}) within the desired processing window, usually around 280°C. At temperatures below T_{ODT}, incompatibility between the PCHE and PE blocks produces microphase separation, into the familiar lamellae, cylindrical, and spherical morphologies (Bates and Fredrickson, 1999) as the PCHE content is increased (or decreased). For optical disks, finding the optimal glass content also was critical, representing a compromise between toughness and stiffness. Once the composition is set, the molecular weight controls T_{ODT}. Above T_{ODT}, the material is a homogeneous melt that is easily processed. Hence, the pentablock architecture overcomes brittleness at low temperature yet facilitates molding at elevated temperatures by exploiting both the ordered and disordered states, respectively.

Recent experimentation has revealed profound differences in the dynamics of CEC vs. CECEC near T_{ODT} (Vigild et al., 2001). These differences can be quite beneficial. For example, the pentablock exhibits superior melt strength, which derives from a higher molecular weight; note, T_{ODT} changes only slightly when CEC is coupled into CECEC. Also, when cooled below T_{ODT}, the pentablock develops a very disorganized morphology with only short-ranged translational order. Unlike diblocks and triblocks (Garetz et al., 1996), the CECEC specimens fail to nucleate large coherent domains, instead freezing in a rather disordered nanoscale structure (see Figure 2). We suspect this effect, which is advantageous to the optical quality and mechanical properties of molded CDs, derives from the restrictions on molecular mobility imposed by the multiblock architecture. Application of shear instantly transforms the material into a single crystal form (see Figure 2).

Scientists and engineers at Dow quickly capitalized on this new technology, scaling up the polymerization and catalytic hydrogenation processes and evaluating the potential for molding CDs. The CECEC pentablocks gave a good overall combination of pattern replication, low birefringence, moisture sensitivity, heat distortion, modulus, and toughness. And the economics looked competitive as well. These materials are now moving to the marketplace, just four years after initial conception in 1997. This year, Dow expects to produce about two million pounds of the optical grade material for market evaluation.

Collaboration

Industry-academic collaboration played a pivotal role in this project. Interactions with the Universities of Minnesota and California brought expertise in block copolymer phase behavior, rheology, and structure/property relationships, dramatically speeding up and focusing the project at Dow. Significantly, these relationships were in place prior to recognizing that the block copolymer architecture represented a potential solution to the technical hurdles thwarting development of PCHE. An important component was Dow's strategic decision to institute technical advisory boards (TABs) in key areas, such as materials science. Glenn Fredrickson's representation on the Materials TAB provided an effective conduit for dissemination of research results from Bates' laboratory into Dow's R&D organization and served to break down initial resistance to the block copolymer concept. When materials and processing challenges arose, university and company scientists and engineers were prepared to address them almost immediately. Along with laboratory research and theoretical support, short courses, sabbaticals, and visits between facilities expedited education of company participants. Dow offered a real plum to the universities. In addition to the enabling catalyst technology, the company provided a focus on markets, along with polymer material and industrial processing requirements. Perhaps, the greatest challenge we faced involved intellectual asset ownership and rights to practice. A workable balance must be struck where the university and company satisfy their institutional needs. Our experience with the pentablock project teaches us to establish quantitative and well-understood intellectual asset agreements upfront. Ultimately, more than any other factor, the success of this new product relied on the free exchange of ideas between the scientists and engineers at all institutions.

While it is still too early to anticipate the totality of the market response to PCHE-based pentablock copolymers, the very attractive property set and processing characteristics lead us to believe that these materials will at the very least be competitive for plastic optical media. We would be surprised if these polymers did not also find many other applications demanding transparency, high heat, and melt processibility—ultimately evolving into a major new class of engineering or even commodity plastics.

Acknowledgments

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