

to molecular weight and molecular weight distribution control, but more so to the possibility of the preparation of terminally functional liquid or rubbery prepolymers (telechelics, macromonomers), and of thermoplastic elastomeric block copolymers by sequential monomer addition. This presentation will focus on developments in the latter areas. In the realm of terminally functional prepolymers, the recent one-post synthesis of a unique allyl-terminated polyisobutylene (PIB) is of particular interest.

In the field of thermoplastic elastomers (TPE) the synthesis of several linear and three-arm star TPE with the general microarchitectures, where glassy denotes high Tg glasses, will be described and discussed. These developments were mainly inspired by Shell's highly successful Kraton materials. Kratons are linear triblocks comprising polystyrene (PS) glassy outer segments and polybutadiene or polyisoprene or hydrogenated polybutadiene (i.e., poly(ethylene-co-1-butene) rubbery inner segments.

The synthesis of PS-PIB-PS or PS-(PIB-PS)-PS has been accomplished by the living carbocationic polymerization of isobutylene initiated by appropriate two (or three) functional

initiating systems followed by the addition of styrene. The product was a TPE with promising mechanical properties.

The strength of TPE is strongly affected by the Tg of the outer glassy segment. With this information in mind, TPE's have been prepared containing relatively high Tg glassy domains.

The copolymerization of styrene derivatives yielding relatively high Tg polymers leads to products whose Tg can be controlled by controlling the overall composition of the copolymer.

The Tg of the glassy segment of the TPE can also be controlled. The synthesis of a representative TPE with random p-tert-butylstyrene/indene copolymer glassy domain will be outlined.

P-Chlorostyrene and p-fluorostyrene, i.e., monomers that heretofore could not be satisfactorily polymerized by other (i.e., anionic) living techniques; have been readily polymerized by living carbocationic methods to high molecular weight products with predictable molecular weights. Subsequently, TPE containing the poly(p-chlorostyrene) is of interest on account of its relatively high Tg (127 °C) and flame resistance.

S. Wolff

Optimized Reinforcing Systems*

The direction of requirements concerning the performance of an article is pre-determined by its desired functionality and service life. These demands are complicated even further by economic, ecological, and toxicological aspects.

The car industry, for instance, requires tires with a long service life, a high degree of driving safety, and low fuel consumption, i.e. tires giving low treadwear, excellent traction on wet and dry surfaces, and low rolling resistance, and if possible all at the same time.

While striving to achieve such goals by changing the compound composition, it is necessary to re-investigate the state of the art with a view to decoupling vulcanizate properties which have so far been considered as being intricately linked. This can be done either by using conventional products or by developing new ones. This applies both to polymers and fillers as the constituents of reinforcing systems.

The only fillers suitable for use in tire treads are active blacks and silicas. This investigation therefore attempts to determine in how far these fillers are able to help solve the above problem.

The major difference between the two filler groups lies in their reinforcing mechanism. The question therefore arises as to whether a combination of different reinforcing mechanism could optimize vulcanizate properties, in particular E*, tan δ , and treadwear, and produce the desired effect.

The reinforcing effect of furnace blacks is caused above all by the adsorption (hardly any covalent bonds) of the polymer on the

accessible surface of the carbon black aggregates and agglomerates. The latter is characterized by 24M4-DBP absorption and CTAB adsorption. Only by including the dispersive component of surface energy γ_s^d is it possible to describe more accurately and for all furnace blacks the dependence of E* and tan δ on carbon black properties, including treadwear.

Silicas are governed by a different reinforcement mechanism.

The low value of the dispersive component of surface energy γ_s^d and the higher value for TEA absorption in the case of the silica are of considerable importance: the lower γ_s^d is responsible for the low abrasion resistance of silica vulcanizates. E* and tan δ , on the other hand, are determined by the presence of a silica network within the rubber matrix, as indicated by the high TEA absorption.

The modification of silicas with bis (3-triethoxysilylpropyl)-tetrasulfane changes their reinforcing mechanism in such a way that the adsorptive rubber bonds at their surface are replaced by covalent rubber-to-filler bonds.

This raises abrasion resistance to the level of N 220, whereas the, for silicas, typically low tan δ -value is maintained or reduced even further.

The right choice of suitable active blacks and silicas, of the blend ratio and the degree of silanization permits the different reinforcing mechanisms to be matched in such a way that E*, tan δ , and treadwear are to a large extent decoupled and can finally be tailored to suit the particular application.

Degussa AG, Wesseling, RFA.

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