Preparation of Brominated Polypentenamer and its Substituted Nitrile Derivative

The hydrohalogenation of unsaturated polymers has been documented in the literature.[1,2] Recent interest in flame retardation in plastics has intensified research into the bromination of unsaturated polymers,[3,4] although the feasibility of utilizing these brominated products as intermediates in the preparation of novel polymers has not been explored. Polypentenamer, an elastomer formed from the metathesis of cyclopentane,[5] has been brominated by hydrogen bromide addition. The dilute solution chemistry of nitrile group substitution of the brominated polypentenamer has also been investigated.

Hydrobromination of the Polypentenamer

The procedure used here was adapted from a technique developed for the bromination of polystyrene–butadiene–polystyrene (ABA) block copolymers.[3] Samples of polypentenamer (M_n = 86,000; M_w = 171,000; η_{inh} = 1.71 dl/g) were obtained through the courtesy of Good Year Tire and Rubber Company. Polypentenamer was dissolved in benzene, precipitated in methanol, and dried in vacuum for two days. A total weight of 24.56 g hydrogen bromide (Matheson Gas Products) was bubbled slowly through 14 ml tetrahydrofuran in a foil-covered 50-ml filtration flask immersed in an ice bath. At this concentration, no additional HBr could be dissolved in the clear yellow-green solution. The HBr–THF solution was then rapidly added to 7.103 g polypentenamer redissolved in 125 ml benzene with magnetic stirring in a foil-covered 500-ml round-bottom flask precooled to 15°C. Mild gas evolution was observed as the solution changed from an initial orange color immediately upon the addition of the bromide to a gradual brownish red. The solution was allowed to equilibrate to room temperature, and stirring was continued for a period of one week.

At approximately 24-hr intervals, 10-ml aliquots of the bromination mixture were removed by pipette, precipitated in methanol, and dried in vacuum for two days at room temperature. The wt-% bromide was determined by elemental analysis, and the value for each sampling is plotted versus reaction time in Figure 1. As shown by this graph, the bromination is essentially complete in 48 hr. At the end of the full seven days, the remaining reaction mixture was added dropwise to methanol and the precipitate was recovered, dissolved in benzene, reprecipitated in methanol, and dried in vacuum at room temperature for two days. This final product contained 32.9 wt-% bromine. The glass transition temperature (T_g), measured on a Perkin-Elmer Model DSC II differential scanning calorimeter at a heating rate of 20°C/min, increased from −88°C for the pure polypentenamer to −21°C for the final brominated product.

The brominated polypentenamer was stored under nitrogen at temperatures ranging from 0° to 15°C. All samples were shielded from light. Under these moderate conditions, signs of bromide elimination and subsequent crosslinking of the polymer were evident after approximately 33 days by partial insolubility of the brominated polymer in benzene. After about seven weeks, the total amount of crosslinked polymer had greatly increased. A sample of the brominated polypentenamer, stored for seven weeks under the above conditions, was allowed to dissolve in benzene with continuous stirring over 24 hr, and the gelled polymer was separated from the soluble portion by filtration through a coarse sintered glass filter (150 ml − 60C) under vacuum. Recoverable precipitate from the soluble fraction represented only about 47% of the total recoverable weight of both fractions. Bromine content for this soluble portion was only 14.7 wt-%, while that for the whole sample before separation had dropped only slightly from 32.9 to 32.3 wt-% since analysis of the freshly brominated product some seven weeks earlier. Subsequent brominations for the nitrile substitution step were conducted under more rapid mixing conditions by use of mechanical paddle stirring (5000 rpm).

Attempts to brominate polypentenamer at allylic carbon sites by techniques employed for low molecular weight compounds[6] have proved unsuccessful. Sufficient N-bromosuccinimide (NBS) to attach on the average one bromine atom per repeat unit was added to a dilute solution of the polypentenamer in methylene chloride (1.6 wt-%). The reaction mixture was heated to reflux (40°C) and was photoinitiated by a 200-W incandescent bulb placed next to the reaction flask. Total gelation occurred in less than 4 hr with no detectable bromination (< 0.05 wt-%).
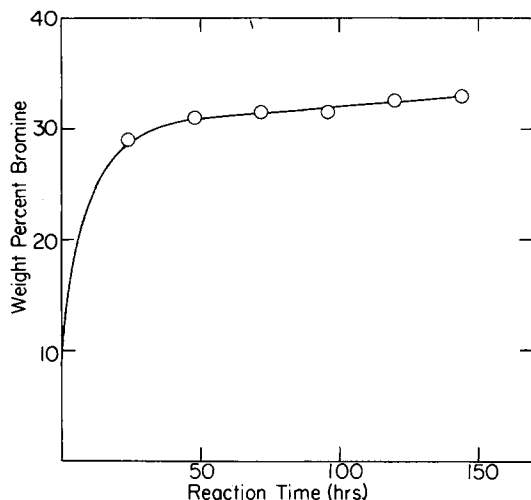
Fig. 1. Weight per cent bromine incorporated into the polypentenamer vs. reaction time.

NITRILE GROUP SUBSTITUTION

Direct substitution of nitrile groups for bromine using inorganic cyanides has been successful for low molecular weight compounds.[7] Nitrile-substituted polypentenamer has been made in this laboratory by Sanui et al.[8] using an aldehyde intermediate prepared by hydroformylation of the polypentenamer. Samples containing in excess of 4 wt-% nitrogen have been prepared in this manner. The direct similarities between these novel polymers and butadiene–acrylonitrile copolymers (NBS rubber) have opened the question whether these modified polypentenamers would show compatibility with poly(vinyl chloride) reported for blends of NBR and PVC (i.e., using the criterion of a single, composition-dependent T_g).[9,10] Since polarity of the pendent nitrile and choride groups is probably the single most important factor in the compatibility of this commercial blend, it is reasonable to expect that a similar concentration of nitrile groups in the polypentenamer would be required. NBR is compatible in all proportions with PVC in the range of 23% to 45% by weight acrylonitrile[10] (6.12 to 11.95 wt-% nitrogen). Polypentenamer with greater than 6% nitrogen content prepared through the hydroformylation route is insoluble and highly unstable. Blends of 3.9 wt-% nitrogen hydroformylated polypentenamer (T_g of $-67°C$ by DSC) coprecipitated from THF solution with PVC in proportions of 25/75, 50/50, and 75/25 by weight were incompatible by DSC. Incompatibility of the NBR/PVC system is also expected when the copolymer of equivalent acrylonitrile content is blended.

To achieve higher nitrogen content, attempts were made to affect direct nitrile substitution of the brominated polypentenamer. At total conversion, nitrile substitution of the 32.9 wt-% bromine containing polypentenamer should reach 7.6 wt-% nitrogen content (in the expected compatibility range).

A dilute solution of a freshly brominated sample of polypentenamer (32.8 wt-% Br) was made by dissolving 1.50 g in 300 ml benzene in a 1-liter, three-neck round-bottom flask fitted with reflux condenser, thermometer, and mechanical stirrer. Slowly, 300 ml dimethyl sulfoxide was added through an addition funnel (10 ml/min) during rapid agitation of the benzene solution (mechanical paddle stirring). The addition of nonsolvent produced a fine suspension of swollen polymer globules. To this mixed solvent solution, a large excess of potassium cyanide (2.50 g) was added. The solution was heated under mild nitrogen purge and the flask was covered with foil. Mild temperatures were employed in all runs to minimize possible crosslinking and thermal degradation of the product. The reaction mixture after each run was added dropwise to a large excess of methanol. The precipitate was filtered, dissolved in THF, reprecipitated in methanol, and dried under vacuum at room temperature for two days before submission for elemental analysis.

Table I summarizes the results for four runs at different temperatures and reaction times.

TABLE I
Conversions in the Nitrile Substitution Reaction

Run no.	Reaction temp, °C	Reaction time, hr	Product composition	
			wt-% N	wt-% Br
1	59 ± 7	186	0.61	25.3
2	72 ± 5	138	1.46	12.6
3	76 ± 4	285	2.29	4.47
4	87 ± 6	116	2.38	2.06

The product material from the lowest temperature reaction (run 1) was completely soluble in benzene and in THF. At higher temperatures and consequently greater conversions, the product became increasingly crosslinked. Product from run 2 could be separated into a soluble portion approximately 42 wt-% of the total recoverable polymer, while that from runs 3 and 4 were soluble to the extent of only about 7% to 10% by weight. Elemental analyses of the soluble and insoluble fractions were remarkably close to the overall product composition indicating the importance of rapid mixing in the bromination step to ensure product homogeneity.

The highest nitrogen content achieved in these runs was 2.4 wt-% (below the 3.9 wt-% sample in the incompatible blend). In this nearly complete substitution (run 4), conversion was only about 33% of theoretical, suggesting competitive elimination of hydrogen bromide and return to higher degrees of unsaturation.

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J. R. FRIED
F. E. KARASZ
W. J. MACKNIGHT

Polymer Science and Engineering and Chemistry Departments,
and Materials Research Laboratory
University of Massachusetts
Amherst, Massachusetts 01002