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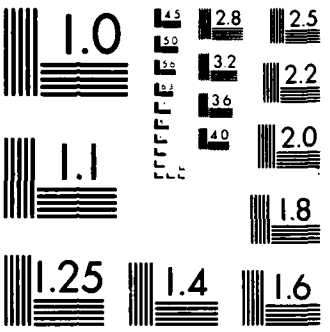
MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND
ENGINEERING J C CHIEN ET AL 01 JUL 87 TR-22
UNCLASSIFIED N00014-85-K-0880 F/G 7/6 NL



OFFICE OF NAVAL RESEARCH

CONTRACT N00014-85-K-0880

Task # NR SDRH 021

Technical Report No. 22

SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMERS

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July 1, 1987

SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMERS

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1. Polyether-Polyimide Block Copolymers

Three series of Polyether-Polyimide (PEPI) block copolymers were synthesized. Soft segments were poly(propylene glycol) (PPO) $M_n^{\square}$ = 2,000 and 4,000. Hard segments were pyromellitic dianhydride (PMDA) and di-(2-hydroxyethyl)-dimethylhydantoin (H). The hard segments were formed from 4,4'-diphenylmethane disocyanate (MDI) with PMDA or 95% PMDA and 5% H. The first series designated as PEPI-2K was synthesized with PPO-2,000, MDI and PMDA. The second series, PEPI-2KH, used PPO-2,000, MDI, 95% PMDA+ 5% H. The third series, PEPI-4K, used PPO-4,000, MDI and PMDA. PEPI copolymers in each series varied by weight percent of hard segment.

IR revealed the correct chemical structure of the PEPI block copolymers. Degree of phase separation was investigated by low temperature DSC which showed the relationship between glass transition temperature of soft segment and hard segment content. Comparing among three series, the PEPI-4K had the lowest T_{gs}. Thus, the degree of phase separation might be in the order of PEPI-4K > PEPI-2K. PEPI-4K using PPO-4,000, having more free movement of the soft segment, migh cause the low T_{gs}. Only PEPI-2K had the hard segment T_{gh}s which were also observed by DMTA. Shorter soft segment length enhanced better crystallinity.

These factors such as phase separation, crystallinity in the hard domain all contribute to polymers' mechanical properties.

Generally, a higher degree of phase separation resulted in higher values of Young's modulus and stress at break. However, the data collected is not enough to demonstrate.

2. Polyacetal-Poly(ethylene glycol) Block Copolymers

A series of block copolymers, polyacetal-poly(ethylene glycol) (PAPEG) has been synthesized. The soft segment, poly(n-butyl-1,3,6-trioxocane); M_n = 1,650, was obtained by cationic condensation of valeraldehyde and diethylene glycol in the presence of p-toluene sulfonic acid. The hard segments composed of MDI and polyethylene glycol (M_n = 3,400; mp = 55°C). By varying the hard segment content, PAPEG copolymes with different properties were obtained.

To distinguish PAPEG polymer from its mixture is the main objective. The PAPEG block copolymers are transparent, yellow, weak materials. Mixture of PAPEG and PEG appear as white dots on yellow matrix. DSC studies not only showed the melting transitions of PAPEG block copolymers, but also the indirect evidence that none or little excess PEG. The crystallinities of PAPEG block copolymers were obtained from the H_f of DSC thermograms. T_gs of the PAPEG copolymers did not change with increasing hard segment content due to good phase separation.

The soft and hard segments of PAPEG block copolymers possessed the same chemical linkage ether and behaved differently. Crystallinity of the hard segment, hydrogen bonding, and polar effect contribute to PAPEG's phase separation.

3. Poly(tetrahydrofuran)-Poly(dioxolane-co-trioxane) Block Copolymers

The poly(tetrahydrofuran)-poly(dioxolane-co-trioxane) (PEPDT) block copolymers were synthesized. The soft segment, poly(tetrahydrofuran), was obtained commercially. Hard segment, PDT, was known as its high crystallinity and acidic sensitivity. Several attempts had been done to obtain a PDT having a melting transition near 100°C. The M_n = 3,700 of PDT was obtained by titration of active hydroxyl end groups. The PEPDT copolymers can be classified into three sub-series, which were coupled by different coupling agents, toluene diisocyanate (T), hexamethylene diisocyanate (H), and adipoyl chloride (A).

PEPDT copolymers showed two-stage pattern of degradation thermally and catalytically. TGA also indicated that first stage of decomposition was due to the PDT under heating and acidolysis. PEPDT exhibited four transitions as detected by DSC, glass transition, cold crystallization, melting of soft block, and melting of hard block. The melting transitions of hard block of PEPDT copolymers were higher than PDT itself that was caused by increasing molecular weights at the first stage of end-capping. The T_gs were not affected by changing the coupling agents and hard segment contents. Thus, the PEPDT block copolymers are phase separated block copolymers.

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