the greatest. This synergism in modulus has been noted before in compatible PPO–PS blends[17] and has been ascribed to an increase in packing density due to blending. One would therefore expect the FIPN's to exhibit the greatest increase in modulus, since there should be a greater amount of permanent chain entanglements between the two networks which would result in a greater increase in packing density. The moduli sharply decrease near the T_g's of each blend, respectively, as usual. The loss modulus E'' of this sample as a function of temperature is also shown in Figure 2. The loss modulus data show a single T_g, indicating extensive phase mixing. The T_g's, however, are broader than those of the pure components.

Experimental Section

A. Preparation of Polymers and Polymer Blends. 1. The PPO was brominated by direct bromination of poly(phenylene oxide) in solution. One liter of *s*-tetrachloroethane and 125.0 g (1.04 mol) of PPO (η = 0.55 dL/g) were combined in a 3-L round-bottomed, three-necked flask equipped with a stirrer, thermometer, dropping funnel, and condenser. The reaction mixture, maintained under a nitrogen atmosphere and illuminated with a sun lamp, was stirred and heated to incipient reflux (136 °C). Bromine (7.86 g, 0.0492 mol) was added dropwise. Copious evolution of HBr carried off some of the bromine, so another equal amount of bromine was added. The reaction was maintained at 136 °C for 1 h and then cooled, and chloroform was added. The brominated PPO was precipitated by slow addition of methanol, filtered, and washed with methanol. The material was dissolved in chloroform and reprecipitated. The collected material was broken up in a Waring blender, filtered, washed well, and dried in vacuo at 60 °C overnight. A master batch of PPO (containing 4.75% bromine) was prepared by dissolving in toluene (20% by weight).

2. Linear Blends. The PPO solution and styrene monomer (inhibitor removed) were mixed with 1% azobis(isobutyronitrile) (AIBN) catalyst. The mixture was poured between glass plates with a Teflon spacer and subsequently polymerized at 70 °C for 24 h. The glass plate mold was kept in a horizontal position so that an even-thickness sheet could be obtained. Combinations of 75, 50, and 25% PPO by weight were made.

3. Pseudo-IPN's (PDIPN's). Two types of pseudo-IPN's were prepared, one from cross-linked PPO (CPPO)/linear polystyrene (LPS) (PDIPN-1) and the other from a linear PPO (LPPO)/cross-linked polystyrene (CPS) (PDIPN-2). The former PDIPN's were prepared from a mixture of PPO solution with ethylenediamine (cross-linking agent) and styrene monomer with AIBN. Ethylenediamine (1.4 g) was added to 40 g of PPO. The mixture of PPO solution and styrene monomer admixed with divinylbenzene and AIBN resulted in PDIPN-2. The curing conditions and compositions were the same as those for the linear blends.

4. Full IPN's (FIPN's). FIPN's (both polymers cross-linked) were prepared from the mixture of the PPO solution with ethylenediamine and stryene monomer with divinylbenzene and AIBN. The curing conditions and compositions were the same as those for the linear blends.

B. Measurements. 1. Electron Micrographs. The samples were prepared according to Kato's osmium tetraoxide staining technique[18] and a two-step sectioning method. The electron micrographs were taken at a magnification of 95 000 with an AEI 6B and a Philips 300 transmitting electron microscope.

2. Differential Scanning Calorimetry. The glass transition temperatures (T_g's) were determined on a DSC-2 Perkin-Elmer differential scanning calorimeter. Measurements were carried out from 300 to 500 K under nitrogen at a scanning rate of 10 °C/min. Specimen sizes were on the order of 20 mg.

3. Ultimate Properties. The tensile strengths were determined on an Instron tensile tester at room temperature at a crosshead speed of 2 in./min, using dumbbell-shaped specimens (0.08 in. × 0.25 in. × 2 in.).

4. Rheovibron. Dynamic viscoelastic properties were measured on a Model DDV-II Rheovibron dynamic viscoelastometer (Toyo Instrument Co.). A frequency of 110 Hz and a heating rate of 2 °C/min were used in taking measurements over a temperature range of 20–260 °C. Nitrogen gas was purged through the sample chamber to avoid oxidation at high temperature.

Acknowledgment. The authors acknowledge with gratitude the support of the National Science Foundation under NSF contract DMR-7805938, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the help of Drs. A. Hay and D. M. White and Mrs. B. M. Boulette of the General Electric Research Center for their synthesis of the brominated PPO.

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Oxyluminescence of Random and Block Copolymers of Styrene and Butadiene

K. NAITO† and T. K. KWEI*

Bell Laboratories, Murray Hill, New Jersey 07974.
Received November 19, 1979

In two previous studies of chemiluminescence of polymers, it was found that the oxyluminescence vs. temperature curve of a polymer exhibited a sharp inflection as the mechanism of the oxidation reaction changed with temperature.[1,2] The study was also extended to polymer mixtures. The luminescence curve of an incompatible mixture retained the characteristics of the component polymers,[2] but only one inflection was observed if the two polymers formed a compatible pair.[1] Furthermore, the inflection temperature of the compatible mixture changed systematically with composition. These results suggest that the proximity of the two different macromolecular chains plays an important role in the luminescent behavior of mixtures.

†Permanent address: Research Division, Bridgestone Tire Co., Tokyo 187, Japan.

0024-9297/80/2213-1018$01.00/0

Table I
Material Properties

material	density, g cm^{-3}	styrene content, wt %	T_g, °C	microstructure[a]
polybutadiene	0.900	0	−93	60% trans
poly(styrene-*co*-butadiene)	0.935	23.5	−63	72% trans
poly(styrene-*co*-butadiene)	0.965	45	−40	~70% trans
SBS block copolymer	0.94	30	−96, 40–50	54% trans, 38% cis, 8% 1,2

[a] Information supplied by manufacturer.

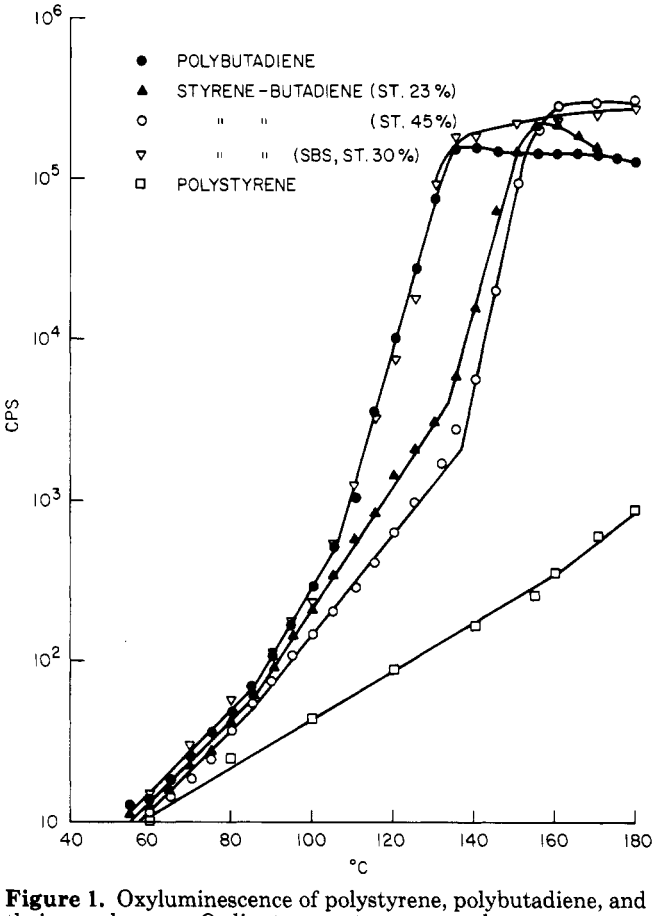

Figure 1. Oxyluminescence of polystyrene, polybutadiene, and their copolymers. Ordinate, counts per second.

It is commonly known that the physical properties of a random copolymer often bear many similarities with those of a compatible blend, and the properties of a block copolymer with those of an incompatible one. To test the applicability of this generalization to the luminescence phenomenon, we have studied random and block copolymers of styrene and butadiene. The latter polymer is much more susceptible to oxidation than polystyrene for which the oxyluminescence data have already been reported by us in an earlier publication.[2]

Experimental Section

Butadiene polymer and copolymers were obtained from Aldrich Chemical Co. The compositions and the properties of these polymers are listed in Table I. Except for the block polymer which was polymerized in solution, the two other polymers were polymerized by an emulsion process. The block length of polystyrene in SBS is $M_n \simeq 1.37 \times 10^5$ and that of polybutadiene is $M_n \simeq 6.34 \times 10^5$.[3]

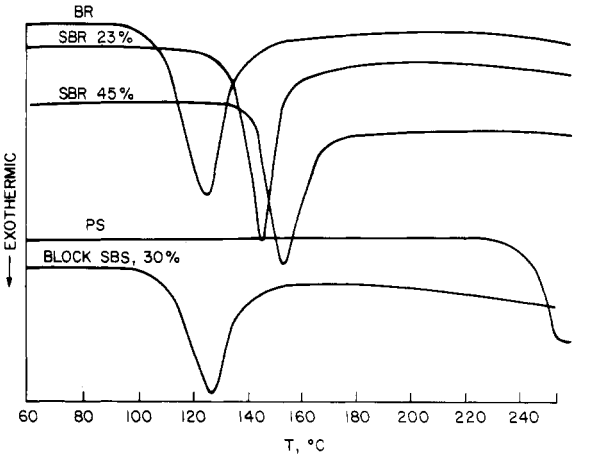

Figure 2. Differential scanning calorimetry of polymers in an oxygen atmosphere.

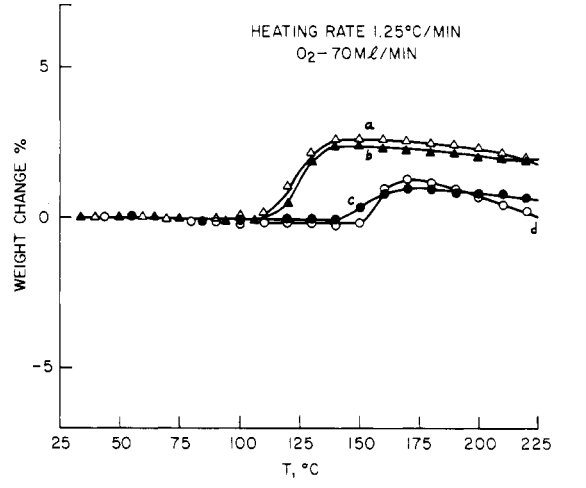

Figure 3. Thermogravimetric analysis of polymers in oxygen: (a) polybutadiene; (b) block copolymer; (c) random copolymer, 23% S; (d) random copolymer, 45% S.

Films of the above polymers were cast from 4% toluene solutions. The solvent was removed by evaporating under nitrogen at room temperature for 1 week and then under vacuum at 60 °C for another week. Oxyluminescence, calorimetric, and thermogravimetric measurements were performed as already described in ref 1 and 2.

Results

The luminescence intensities of polystyrene, polybutadiene, and their copolymers have been measured from 40 to 180 °C and are shown in Figure 1. The curve for polystyrene has been presented earlier and needs no further discussion.[1] The intensities of the emulsion-polymerized polybutadiene differ from the values obtained for *cis*-polybutadiene[2] because the oxidation of PB is sensitive to the microstructure of the chain. But the same interpretation is applicable, at least qualitatively, to both polymers. The luminescence curve shows an inflection at 105 °C and reaches a plateau later at about 135 °C. The inflection at 105 °C coincides with the onset of the exotherm in the differential scanning calorimetric experiment (Figure 2) and also with the beginning of the weight increase in a thermogravimetric experiment. The formation of peroxide compounds with attendant cross-links and cyclic structures becomes increasingly important at this temperature.[4] On the other hand, the leveling off of luminescence intensities at 135 °C parallels the beginning

of weight loss in TGA. The fragmentation of the PB chain has now become predominant.[4] These explanations have been offered by us in ref 2.

When the luminescence emissions of the two random copolymers are compared with those of PB, we see that the intensity at a given temperature decreases with decreasing butadiene content. Furthermore, the inflection points shift to about 130 °C (Figure 1). These inflection temperatures again agree approximately with the onsets of DSC exotherm and of weight gain in TGA. We note that a shift in the inflection temperature with composition has also been observed in compatible mixtures of PS and poly(vinyl methyl ether).[2] At higher temperatures, the plateau or the broad maximum reached in the luminescence curves at 155 to 160 °C likewise coincides reasonably well with weight loss data.

For the block copolymer, the DSC and TGA results resemble closely those of polybutadiene. The luminescence curves of the two polymers are indistinguishable except at temperatures above 135 °C. The similarity between the luminescent behavior of the block polymer and the polybutadiene suggests that the surface composition of the block copolymer resemble that of polybutadiene.

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Effect of Main-Chain Length and Nature of Side Chain on Specific Heat Variations of Polypeptides

PIERRE DELHAES,*[1a] JEAN-PIERRE MANCEAU,*[1a] and CLAUDIO TONIOLO[1b]

Centre de Recherche Paul Pascal, CNRS, Domaine Universitaire, 33405 Talence, France, and Biopolymer Research Center, CNR, Institute of Organic Chemistry, University of Padua, 35100 Padua, Italy.
Received January 31, 1979

Specific heat measurements at low temperatures, where only the acoustic modes are appreciably excited thermally, can give valuable information about the solid-state structure of macromolecules. By this method the conformation of polypeptides can be ascertained[2-5] and, in particular, an estimate of the proportion of α to β structure may be obtained.[6]

In this context, we have[2,3] recently demonstrated that L-valine, L-alanine, and tri(L-alanine) present a specific heat variation characteristic of a tridimensional molecular solid which is correctly fit by the Kitaigorodskii empirical rule.[7] For the L-valine and L-alanine homopolypeptides in the β form the predicted three- and two-dimensional vibrational behaviors, due to the intermolecular hydrogen bondings responsible for the sheet structure, were observed. For the α form of poly(L-alanine), conversely, a one-dimensional pattern at higher temperature was shown, since each polypeptide chain vibrates separately. The Debye–Tarasov model[8] accounts well for the experimental results of all polypeptides.

In this note we report the specific heat variations of two *monodispersed* homooligopeptides of the L-valine and L-alanine series, namely, *t*-Boc-(L-Val)$_6$-OMe and *t*-Boc-(L-Ala)$_6$-OMe (*t*-Boc = *tert*-butyloxycarbonyl, OMe = methoxy). We hoped the intermediate molecular weight

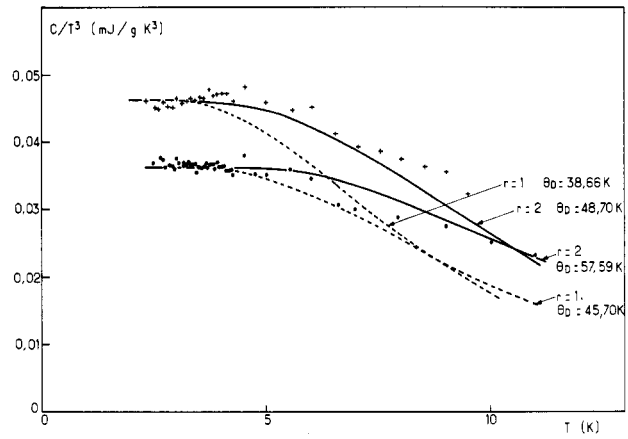

Figure 1. Specific heat divided by the cube of temperature vs. temperature for *t*-Boc-(L-Val)$_6$-OMe (+) and *t*-Boc-(L-Ala)$_6$-OMe (●). Dashed lines represent the standard Debye law (r = 1) and solid lines the Kitaigorodskii model (r = 2).

of the two peptides would allow us to obtain deeper insight into the effect of the main-chain length on the long-range order of polypeptides in the solid state.[2] In addition, comparison of the identical main-chain-length homopeptides derived from L-valine, containing a β-branched side chain, and L-alanine, characterized by a small and linear side chain, would allow the effect of the bulkiness of the lateral group of the constituent amino acid residue to be investigated.[3]

The details of the synthesis of *t*-Boc-(L-Val)$_6$-OMe and *t*-Boc-(L-Ala)$_6$-OMe are reported in ref 9 and 10, respectively. Rigorously monodispersed, chemically and optically pure, solvent-free, and well-crystallized homooligopeptides were obtained. The samples present a cross-β structure with a defined unit cell, as shown by recent crystallographic work.[11,12] The heat capacity was measured between 2 and 10 K by a standard adiabatic method on a small polycrystalline sample as previously described.[2] The two hexapeptides were compressed to give a pellet which was placed on an alumina disk. The heat capacity of the experimental set up, i.e., alumina disk, germanium thermometer, constantan pressure gauge used as a resistor, and GE 7031 glue, was determined in a previous experiment. The heat capacity of the compounds was obtained by difference between the full and the empty cells which is around 50% of the empty cell with a mean accuracy of about 5%. The two hexapeptides after compression and thermal treatment are still in the β form,[13] as verified by infrared absorption spectroscopy.

The experimental results in the form of the usual $C_p/T^3 = f(T)$ plot are presented in Figure 1. In both cases a broad maximum followed by a monotonous decrease is found. At low temperatures the Debye law for tridimensional phonons gives the standard relation

$$C = {}^{12}/_{5} r R \pi^4 (T/\theta_D)^3$$

where C is the heat capacity per mole, R is the ideal gas constant, r is the number of vibrators, and θ_D is the Debye temperature.

To fit the experimental data we can employ the usual Debye approximation for atomic solids which takes into consideration the acoustic modes only (r = 1; see Figure 1).

However, to get a better fit we can apply the Kitaigorodskii molecular method, which takes into account six degrees of freedom for each molecule, three translations, and three rotations, approximated by the same Debye function, with the number of vibrators r = 2 per unit cell. As already shown for small peptides a better agreement

0024-9297/80/2213-1020$01.00/0