

NATURAL RUBBER/POLYSTYRENE SEGMENTED COPOLYMERS BY GAMMA RADIATION TECHNIQUE: STRUCTURAL CHARACTERISTICS STUDIES

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Abstract. Natural rubber/polystyrene segmented copolymers were synthesized from acrylated liquid natural rubber as the soft segment and styrene monomer as the hard segment with various compositions of hard and soft segments by gamma radiation polymerization. Structural features of the segmented copolymers formed were characterized by infrared and nuclear magnetic resonance spectroscopy analysis. The existence of absorption bands at 2962, 2928, 2855, 1664, 1450, 1378 and 838 cm^{-1} show major characteristics of natural rubber in the segmented copolymer. Peaks at 3058 and 3024 cm^{-1} indicated the existence of benzene aromatic ring. The absorption bands at 2919 and 2848 cm^{-1} show the asymmetry and symmetry stretching of $-\text{CH}_2-$ for polystyrene. The ^1H and ^{13}C NMR spectra also exhibit all the features of acrylated liquid natural rubber as the soft segment and polystyrene as the hard segment indicating that the copolymers made up of the two segments.

Keywords: segmented copolymers, liquid natural rubber, and radiation polymerization

1. Introduction

Segmented copolymers comprising glassy and rubbery microdomains are used as thermoplastic elastomers [1]. Segmented copolymers consist of elastic and flexible soft segments and hard segments. The glass transition temperature of the hard segments is much higher than that of the soft segments, so the hard segments act as the physical crosslinks and the soft segments retain rubber elasticity between glass transition temperatures corresponding to soft and hard segments [2]. Various concentrations of hard and soft segments contents affect the properties of segmented copolymer [3,4,5]. In this present work, segmented copolymers were prepared from acrylated liquid natural rubber (ALNR) as the soft segment and polystyrene as the hard segment with various content of the two segments. The copolymers were synthesized by radiation polymerization technique using gamma ray.

2. Experimental

2.1 Materials

Natural rubber, SMR-L supplied by Guthrie Corp. (M) was used in this experiment. Other chemicals such as toluene (industrial grade), methanol (96%, Scharlau), ethanol (96%, Scharlau), acryloyl chloride (96%, Aldrich), styrene (99%, Aldrich), divinylbenzene (99%, Fluka), sodium borohydride (99%, Aldrich), magnesium sulfate (99%, Aldrich) and sodium chloride (99%, Scharlau) were used as received. Tetrahydrofuran (96%, Scharlau) and triethylamine (99%, Aldrich) were dried with magnesium sulfate before used.

2.2 Preparation of Hydroxyl-terminated Liquid Natural Rubber

Liquid Natural Rubber (LNR), $M_w \approx 14,000$ was synthesized by photochemical method. NR solution was irradiated by a medium pressure mercury lamp (supplied by Photochemical Reactors

Ltd. U.K) for 40 hours in a 5-Liter capacity reactor flask. LNR was treated with sodium borohydride (NaBH_4) as a reduction agent according to Hussin, 1995 [6]. 2% w/v alcoholic NaBH_4 solution was added dropwise at room temperature and was heat up to $\pm 50^\circ\text{C}$ for two hours. 10% v/v sulfuric acid aqueous was added to remove unreacted NaBH_4 and washed with distilled water. Then, the rubber solution was dried overnight with anhydrous magnesium sulfate. The rubber solution was filtered, evaporated and dried in vacuum oven to give a viscous yellowish hydroxyl-terminated liquid natural rubber (HTNR).

2.4 Preparation of Acrylated Liquid Natural Rubber

Acrylated liquid natural rubber (ALNR) was carried out by the reaction of HTNR and acryloyl chloride in dry THF solution [7]. A certain amount of acryloyl chloride and dry triethylamine (catalyst) were added by syringe to the rubber solution at -42°C . Then, the mixture was heated up slowly to room temperature and left to react for 42 hours under argon atmosphere. The reaction was stopped by adding slowly a small amount of distilled water. The liquid rubber yielded was washed with saturated sodium chloride aqueous and distilled water. The product was evaporated and dried in vacuum oven.

2.5 Preparation of Segmented Copolymer

A desired amount of ALNR was dissolved in a desired amount of styrene monomer to form segmented copolymer. The mixture was stirred homogeneously and then poured in a petry dish to give a thickness of ~ 1 mm. The solution was irradiated by gamma ray at a dose of 200 kGy. The copolymer formed was recovered by extraction to remove unreacted monomers and dried to a constant weight.

2.6 Polymer Designation

The samples have been designated as follows. As an example, NR/PS: 20/80 means that the sample contains 20% by weight of ALNR and 20% by weight of polystyrene. The compositions of the copolymer are NR/PS: 20/80, NR/PS: 40/60, NR/PS: 50/50 and NR/PS: 60/40.

2.7 Measurements

Infrared spectra of the segmented copolymers were recorded on a Perkin Elmer FTIR V2000 spectrometer. The ^1H and ^{13}C nuclear magnetic resonance were recorded on a UNITY INOVATM 400 spectrometer.

3. Results and Discussion

3.1 IR Spectroscopy

Figure 1 shows the IR spectra of NR, LNR, HLNR and ALNR. All the spectra of liquid rubbers show major characteristics of NR at 2962, 2928, 2855, 1664, 1450, 1378 and 838 cm^{-1} [8]. The existence of absorption bands at 3400 and 1720 cm^{-1} indicates the hydroxyl and carbonyl groups on the LNR chain. There is a shoulder at the broad $-\text{OH}$ peak at 3315 cm^{-1} shows the present of $-\text{OOH}$ group in the LNR chain. However, the absent of $-\text{OOH}$ band shows the reaction of reduction agent NaBH_4 . The HTNR spectrum with a broad peak at 3429 cm^{-1} indicates the present of hydroxyl group. The ALNR spectrum shows major changes with the absorption bands at 1260 and 802 cm^{-1} , indicates the existence of acrylic group double bond, $\text{C}=\text{C}$ and $\text{C}(\text{O})=\text{O}$ stretching in the acrylic group respectively [9]. The absent of hydroxyl group on the ALNR spectrum shows that the reaction of $-\text{OH}$ group and acryloyl chloride was almost completed.

Figure 2 shows the spectra of ALNR, polystyrene and segmented copolymer. The segmented copolymer formed shows all the structural characteristics of the two main components, ALNR and PS. Peaks at 3058 and 3024 cm^{-1} indicated the existence of benzene aromatic ring [10]. The absorption bands at 2919 and 2848 cm^{-1} show the asymmetry and symmetry stretching of $-\text{CH}_2$ for polystyrene. The present of peaks at 1600 and 1492 cm^{-1} indicated the stretching vibration in plane of vinyl double bond, $\text{C}=\text{C}$ and vibration of benzene ring respectively [11].

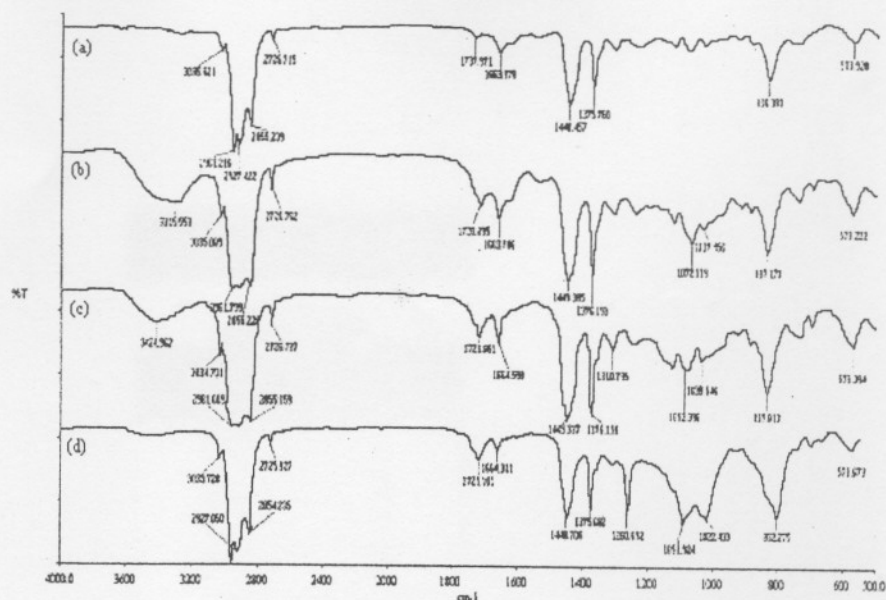


Figure 1. IR spectra of (a) NR, (b) LNR, (c) HLNR and (d) ALNR

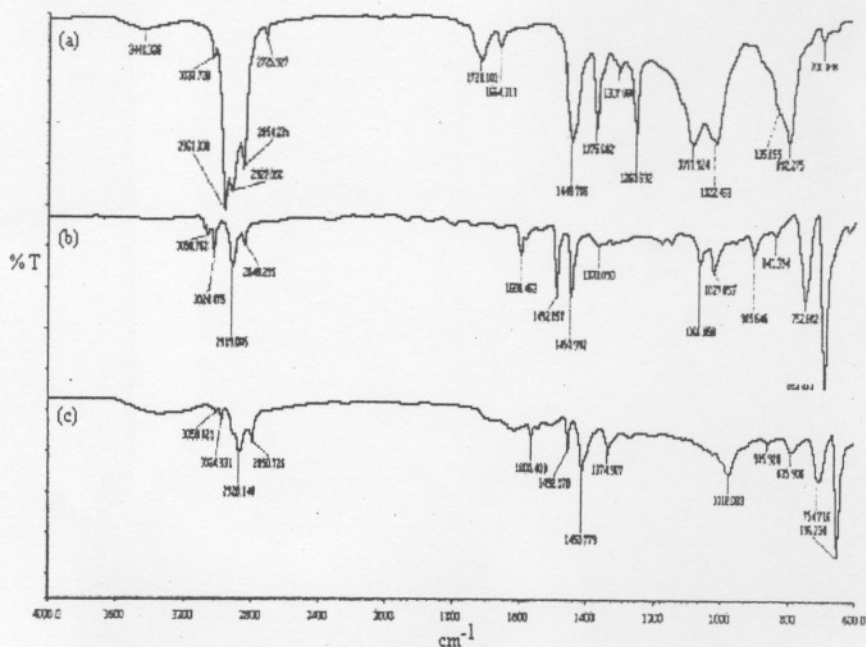


Figure 2. IR spectra of (a) ALNR, (b) polystyrene and (c) segmented copolymer

3.2 NMR Spectroscopy

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the segmented copolymer support the IR spectra in characterizing the features of the soft and hard segments. The NMR spectra of copolymers are found to be identical. Figure 3 and Figure 4 show the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of NR/PS:20/80 respectively, which include all the features of the hard and soft segments. The presence of chemical shifts (δ) at 5.1, 2.06, 2.1 and 1.65 ppm in the ^1H NMR spectrum indicated the existence of methane protons in $-\text{C}(\text{CH}_3)=\text{CH}-$, methylene protons in $-\text{CH}_2\text{CH}_2-$ and methyl protons in $-\text{C}(\text{CH}_3)=\text{CH}-$ respectively, show the characteristics of NR in the segmented copolymers [6,12]. The features of PS were characterized by the existence of δ at 6.3 – 7.2 ppm

indicated the presence of aromatic protons of styrene repeat units [13]. The presence of NR in the segmented copolymers are indicated also in the ^{13}C NMR spectrum at 23.4, 26.6, 32.2, 124.9 and 135.1 ppm which are attributed to the methyl carbon in $-\text{C}(\underline{\text{C}}\text{H}_3)=\text{CH}-$, methylene carbon in $-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}\underline{\text{C}}\text{H}_2-$, methylene carbon in $-\underline{\text{C}}\text{H}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-$, methane carbon in $-\text{C}(\text{CH}_3)=\underline{\text{C}}\text{H}-$ and quaternary carbon in $-\underline{\text{C}}(\text{CH}_3)=\text{CH}-$ respectively. The signals between 125 - 129 ppm and 144 - 146 ppm arise from the aromatic styrene repeat unit [14].

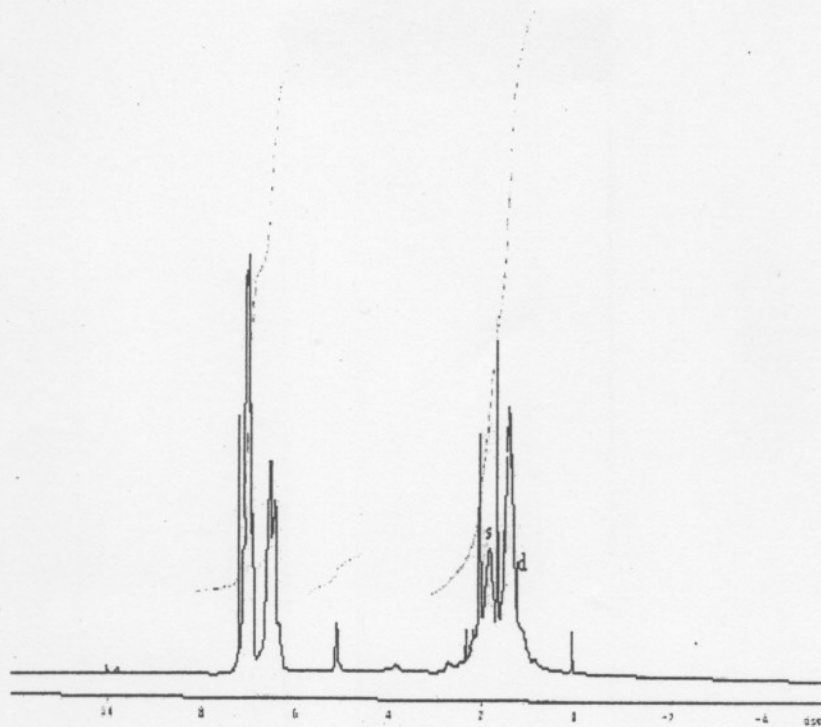


Figure 3. ^1H -NMR spectrum of segmented copolymer

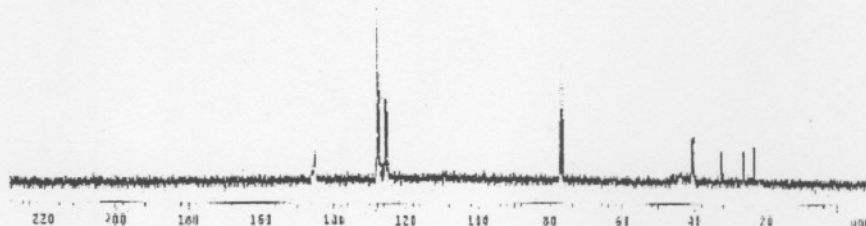


Figure 4. ^{13}C -NMR spectrum of segmented copolymer

Conclusion

Segmented copolymers derived from this present work show all the structural characteristics of ALNR as the soft segment and polystyrene as the hard segment by the IR spectra. The existence of these two segments was also confirmed the presence of signals from ^1H and ^{13}C NMR spectroscopy.

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