Studies on selected polymeric materials using the photoacoustic spectroscopic technique

Hukum Singh†

School of Engineering and Technology, ITM University, Gurgaon-122 017, India

(Received 25 October 2010; revised manuscript received 14 January 2011)

Polymethylmethacrylate–graft–polybisphenol–A-carbonate (PMMA-G-PC) with 50% grafting is synthesized. The graft co-polymerization of methylmethacrylate (0.036 mol · lit^{-1}) onto polybisphenol–A-carbonate (0.5 g) in the presence of a redox couple formed from potassium persulphate (40 mol · lit^{-1}) and thio-urea (30 mmol · lit^{-1}) in aqueous nitric acid (0.18 M, 100 ml) in air at (45±2) °C for 3.0 h. Condensation of (PMMA-G-PC) with N- [p-(carboxyl phenyl amino acetic acid)] hydrazide (PCPH) affords polybisphenol-A-carbonate-graft-polymethylmethacrylate hydrazide (PCGH). The photoacoustic (PA) spectra of (PCGH) are recorded in a wavelength range from 200 nm to 800 nm at a modulation frequency of 22 Hz, and compared with those of pure polybisphenol-A-carbonate (PC), (PMMA-G-PC) and (PCPH). In the present work, a non-destructive and non-contact analytical method, namely the photoacoustic technique, is successfully implemented for optical and thermal characterization of selected polymeric materials. The indigenous PA spectrometer used in the present study consists of a 300-W xenon arc lamp, a lock-in amplifier, a chopper, a (1/8)-m monochromator controlled by computer and a home-made PA cell.

Keywords: photoacoustic, PCPH, PCGH, PMMA

PACS: 78.20.Pa, 78.20.nb **DOI:** 10.1088/1674-1056/20/6/067803

1. Introduction

Thermo set materials such as PC cannot easily be subjected to melt processing in order to fabricate them into articles. However, thermoplastic materials like PMMA require low processing temperatures and as a result can be conventionally processed. Thus, graft co-polymerization of a thermoplastic material makes it suitable for melt processing. Furthermore, a graft polycarbonate with polymethylmethacrylate hydrazide linkages may be used as a high temperature resistant material for aerospace and defense applications. Extensive investigation of the literature has revealed that no attempts have been made to synthesize a graft polycarbonate with such a hydrazide linkage. Therefore, in the present work, we attept[1] to synthesize the polybisphenol-A-carbonate-graft-polymethylmethacrylate hydrazide (PCGH) through condensation of (PMMA-G-PC) 50% and N- [p-(carboxyphenyl amino acetic acid) hydrazide (PCPH) and investigate its optical property using a photoacoustic technique.

2. Experimental

2.1. Starting materials

All the monomers and polymers employed in the present investigation are purchased from M/s. Sigma Aldrich Co. (1001 West Saint Paul Avenue, USA). Other chemicals and solvents used are purchased from M/s S. D. Fine Chemicals, India. Methylmethacrylate was purified by repeated extractions with 10% (w/w) aqueous sodium hydroxide, followed by washing with distilled water. The fraction with a density of 0.942 gcc^{-1} was collected and utilized for all of the graft co-polymerization reactions.

2.2. Synthesis of phenyl glycine-4-carboxylic acid hydrazide

The 4-amino benzoic acid (0.1 mol) in water (200 ml) in the presence of sodium carbonate (22.0 g) and chloroacetic acid (0.1 mol) was refluxed in an air condenser for 3.0 h. The content was cooled and neutralized by concentrated HCL, where N- [p-(carboxyl amino) acetic acid was precipitated. It was crystallized from hot water and dried at 50 °C, melting point 218 °C, yield 87% $C_9H_9NO_4$.[2] The dicarboxylic acid

†Corresponding author. E-mail: hukumsingh@itmindia.edu

© 2011 Chinese Physical Society and IOP Publishing Ltd

(0.1 mol) was esterified by refluxing with dry ethanol (250 ml) in the presence of a certain amount of catalyst of the concentrated sulphuric acid. The product was isolated by neutralizing the reaction mixture with aqueous sodium bicarbonate (10%) to yield ethyl-N-[p-(carboxy phenyl] amino acetate (II), melting point 890 °C, yield 60%. The N- [p-(carboxy phenyl amino acetic acid)] hydrazide (PCPH) was synthesized by refluxing the diester (II) with hydrazine hydrate (98%, 0.1 mol) in ethanol. The crude crystals of (PCPH) were isolated on cooling the reaction medium and crystallized from dimethyl acetamide, melting point 260 °C.

2.3. Synthesis of graft copolymers

In a three-necked flask (250 ml), equipped with dropping funnel, mechanical stirrer and air supply tap, was placed the polybisphenol–A-carbonate 0.5-g potassium persulphate (40 mmol $\cdot$ lit^{-1}) thiourea (30 mmol $\cdot$ lit^{-1}) and the aqueous nitric acid (100 mol, 0.18 M) was introduced followed by initiator potassium persulphate (KPS) into a well dispersed polybisphenol–A-carbonate (0.5 g) in 100 ml of water with continuous stirring at (45±2) °C. At the same time the methylmethacrylate (0.036 mole $\cdot$ lit^{-1}) was added drop wise into the reaction mixture at 1500 rpm for 3.0 h. At the end of the reaction, an excess of methanol was added to quench it. The graft copolymer was purified through repeated extraction with acetone, using a soxlet extractor to remove the homo polymer formed during the reaction. The graft copolymer was isolated and dried at 50 °C.

2.4. Synthesis of PCGH

The PMMA-G-PC (0.5 g) was refluxed with (0.015 mol, PCGH) in N, N dimethyl acetamide (25 mol) at 200 °C for 4.0 h. The polybisphenol-A-carbonate-graft polymethylmethacrylate hydrazide (PCGH) was isolated by its precipitation from the water, filtered and washed with ethanol, and finally dried at 50 °C.

2.5. Experiment

A schematic diagram of the single beam photoacoustic spectrometer designed and developed in our laboratory, which was used to record the photoacoustic spectra of the samples, is shown in Fig. 1.[3] The photoacoustic spectra of all the compounds were obtained in a range of 200 nm–800 nm. A 300-W high pressure xenon arc lamp (Model 68083, Thermo Oriel Corporation, USA) served as an excitation source. The white light was modulated at 22 Hz by a mechanical chopper (SR 540 Stanford, USA). The light was focused through a quartz lens of focal length 4.5 cm on the entrance slit of a (1/8) m monochromator (Cornerstone 130 Model 74000, Thermo Oriel Corporation, USA), which was monitored by a computer using TRACQ 32 and monoutility programs. The dispersed light from the monochromator was focused using a quartz lens of 5.0 cm focal length on a home-made PA cell (2.0 cm in diameter, 2.0 mm in depth). The acoustic signal was detected by a condenser microphone (Radio Shake, USA) mounted in the PA cell. The output of the microphone was amplified by a preamplifier and then finally fed to a lock-in amplifier (SR 530, Stanford, USA) for the digital output display of the amplitude and phase angle. The reference signal was provided to the lock-in amplifier from the chopper for phase-sensitive detection. The time constant of the lock-in amplifier in the present study was 30 s. Since the intensity of the light output from the xenon arc lamp varies over the spectral region of interest, the PA signal from the sample was normalized against a totally light absorbing reference sample like carbon black. In the present study the normalization was performed by dividing the amplitude of PA signal of the sample by the amplitude of PA signal obtained from the carbon black sample.

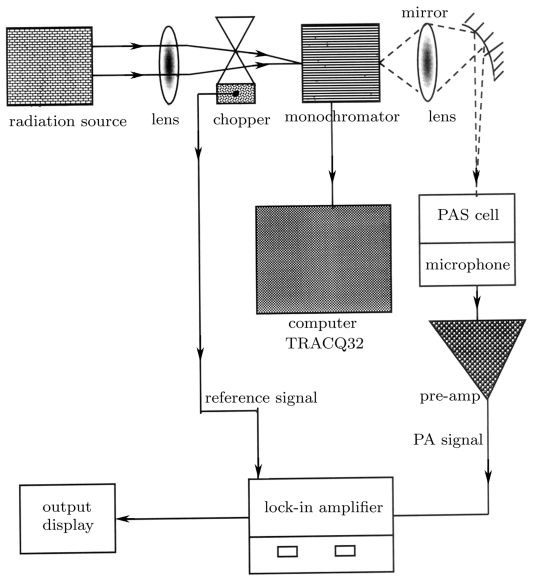


Fig. 1. Schematic diagram of the single beam photoacoustic spectrometer.

3. Results and discussion

The synthesis of PCGH represented by stepwise reaction is shown in Fig. 2. To explain the absorption spectra of PCGH, it is necessary to have the PA spectra of its constituents {PCPH and (PMMA-G-PC) 50%}. Therefore, the first step is to record the PA spectra of PCPH along with its constituents (4-aminobenzoic acid, N- [p-(carboxyl amino) acetic acid], as shown in Fig. 3. It is clearly seen from Fig. 3 that the PA spectra of 4-aminobenzoic acid give three clear absorption bands at 270, 310 and 370 nm separately. Saturated carbonyl compounds such as acetones exhibit three bands: a weak band around 280 nm and a more intense band around 190 nm (not shown in the figure), which are assigned to the $n \rightarrow \pi*$ and $n \rightarrow \sigma*$ transitions, respectively. The $n \rightarrow \pi*$ transitions of a large number of carbonyl derivatives have been reported in Ref. [4]. The band at 270 nm indicates the presence of –COOH-linkage.[5] The present compound (4-amino benzoic acid) has an auxochromic group (–OH) directly linked with the –C=O-centre due to which the (C=O) absorption band at 190 nm is shifted to 270 nm. The second band at 310 nm is due to the presence of $–NH_2$-linkage.[6] When the two substituents are complementary (ortho-para directing versus m-directing) a very large bathochromic shift of 200 nm occurs. Complementary disubsitution seems to have a greater effect on the para position.[7] In the case of N-para carboxylic phenyl amino acetic acid, absorption at 370 nm is observed and phenylalanine gives an absorption band at 250 nm.[6] Comparison between N-carboxylic phenyl acetic acid and phenylalanine indicates that the former can be considered as a para carboxyl derivative of the latter. A large bathochromic shift of 200 nm is observed due to the presence of a complementary group. Therefore a band at 250 nm in p-carboxyl phenyl amino acetic acid is found to be shifted to 370 nm, which is a bathochromic shift of around 120 nm. The band at 270 nm is N- [p-carboxyl amino) acetic acid] and is due to the absorption band of the carboxylic group, which is also observed in 4-aminobenzoic acid. The PA spectra of the hydrazide derivative of N- [p-(carboxyl amino) acetic acid] (PCPH) indicate a missing absorption band corresponding to a –COOH-group at 270 nm. This is because in PCPH free carboxylic is absent. Further, PCPH shows a wide band around 250 nm. Semicarbazide shows an absorption band at 230 nm.[8] This indicates that the absorption at 250 nm in PCPH is due to hydrazide linkage. The very weak absorption band at 290 nm in PCPH may be due to a trace signal of residual para amino benzoic acid remaining unreacted during the synthesis of hydrazide. A similar residual band is also present at 300 nm for compound N- [p-carboxyl amino) acetic acid].

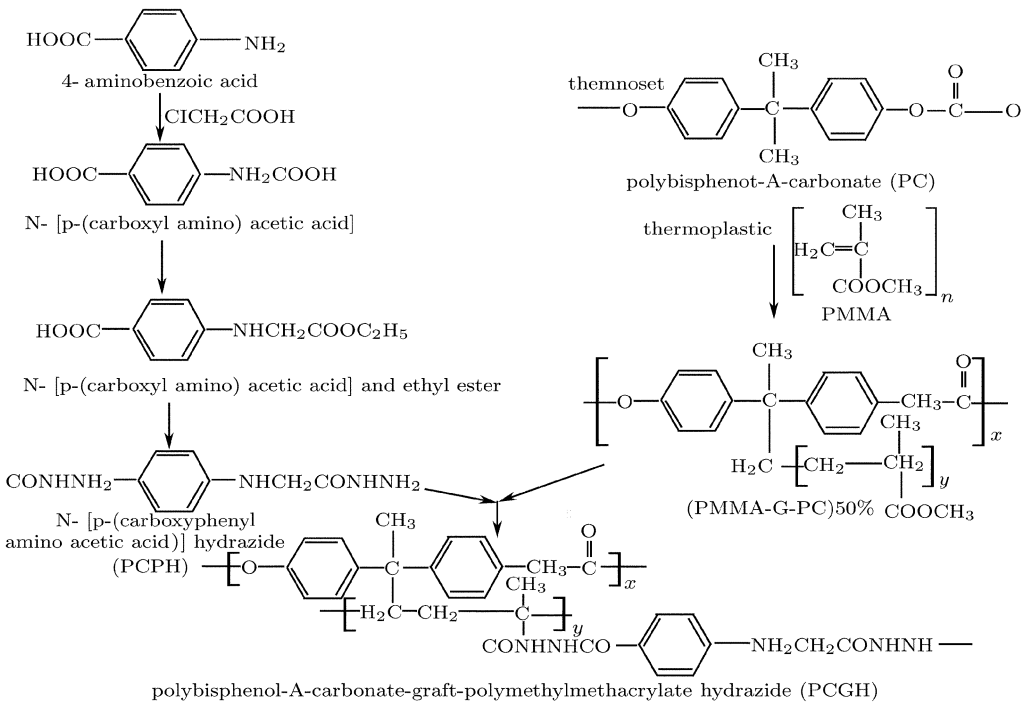


Fig. 2. Various chemical reactions involved in 4-amino benzoic acid, N-[p-(carboxyl amino) acetic acid], N-[p-(carboxyl amino) acetic acid] and ethyl ester, N-[p-(carboxyl amino) acetic acid] hydrazide (PCPH), polybisphenol-A-carbonate (PC), PMMA, (PMMA-G-PC) 50% and polybisphenol-A-carbonate-graft-polymethylmethacrylate hydrazide (PCGH).

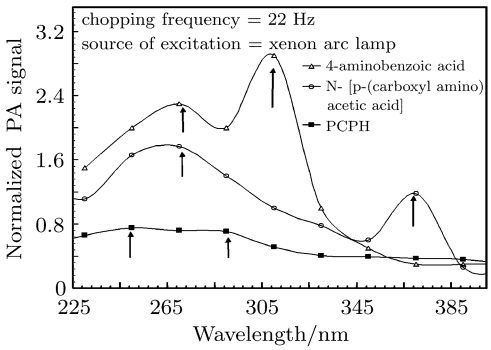


Fig. 3. PA spectra of 4-aminobenzoic acid, N- [p-(carboxyl amino) acetic acid and PCPH polymers.

In the second step the photoacoustic spectra of pure PC, pure PMMA and PMMA-G-PC (50%) are recorded in solid phase and are shown in Fig. 4. It is clear from Fig. 4 that pure PC and pure PMMA present absorption bands at 290 nm and 270 nm, respectively. The peak at 270 nm in the PA spectrum of PMMA may be attributed to the $n \rightarrow \pi*$ transition of the C=O bond.[9] The PA spectrum of (PMMA-G-PC) 50% shows a strong band at 282 nm and its signal strength is large in comparison with pure PC and PMMA. The peak at 282 nm in 50% graft copolymer lies between the peaks of PMMA (270 nm) and PC (290 nm). The experimental observation clearly demonstrates that the PAS technique is able to characterize the graft copolymer with similar groups in their backbone and side chain.

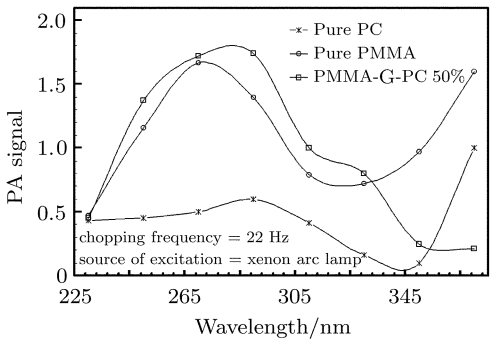


Fig. 4. PA Spectra of PC, PMMA and PMMA-G-PC (50%) graft copolymer.

In the final step the PA spectra of PCPH, (PMMA-G-PC) 50% and PCGH are recorded in a similar condition to that in step 1 and step 2, and they are shown in Fig. 5. It is clearly shown from Fig. 5 that the PA spectra of PCGH are very similar to the PA spectra of PMMA-G-PC, as PCGH shows an absorption band at 280 nm, similar to (PMMA-G-PC) 50%. This is because the backbones of PCGH and PMMA-G-PC have similar bisphenol-A linkages as repeating units. Condensation of PMMA-G-PC with PCPH results in PCGH, having hydrazide linkage as a side chain in the graft copolymer is called polybisphenol-A-carbonate–G-polymethylmethacrylate hydrazide (PCPH). A Fourier transform infrared spectra is shown in Fig. 6. The structure of the proposed side chain in PCGH is also confirmed by the PA spectra in Fig. 5, where similar trends in the PA signals of PCPH and PCGH are observed around 290 nm–330 nm. The FTIR spectra of PCPH and PCGH show C–H bending absorption at 1950 cm^{-1} and C–O stretch absorption at 3100 cm^{-1}. It is clear from Fig. 6 that there are no apparent changes of absorption frequencies in FTIR spectra of PCPH and graft copolymer (PCGH). The overall transmittance of the graft copolymer is increased in comparison with that of PCPH. This result shows that the graft product has become transparent, which is confirmed by its physical appearance and also by the PAS technique. It is concluded from the above observation that FTIR spectroscopy is apparently not applicable to the characterization of these graft copolymers with similar groups in their backbone and side chain.

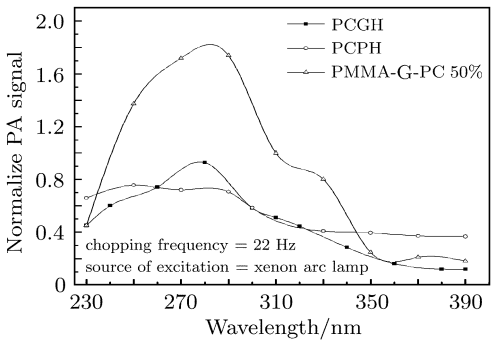


Fig. 5. Photoacoustic spectra of PCPH, (PMMA-G-PC) 50% and PCGH.

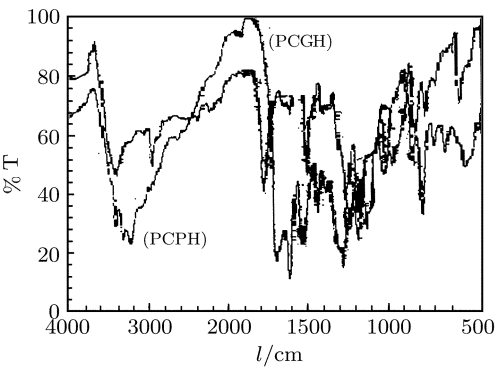


Fig. 6. Combined FTIR spectra of N-[p-(carboxyl amino) acetic acid] hydrazide (PCPH) and polybisphenol-A-carbonate-graft-polymethylmethacrylate hydrazide (PCGH).

The overall absorptions of electromagnetic radiation in PC, PMMA-G-PC and PCGH are ascertained through the heights of the PAS signals. The lower values of PAS signals are assigned to the transparency of the sample. In this regard, the graft co-polymerization of PMMA onto PC increases the PA signal intensity from 0.5 mV to 1.7 mV (figure 5 indicates that the graft co-polymerization of PMMA onto PC reduces the transparency of the latter). Condensation of PCPH with PMMA-G-PC surprisedly reduces the PAS signal from 1.7 mV to 0.8 mV. The above results reveal that PCGH is more transparent than (PMMA-G-PC) 50% and such a result is also observed in FTIR (Fig. 6). The heat resistance of a material depends on the cohesive energy of the bonds.[10] Of this series, the –COOH-linkage indicates that the highest value of cohesive energy corresponds to high melting points[10] In the same way, the introduction of hydrazide linkage may increase the melting point and hence heat resistance of the PCGH. From these observations it follows that PCGH possesses high heat resistance and less reduced transparency than its parent polymer. Therefore, materials such as PCGH may be utilized as aerospace materials for defense purpose.

4. Conclusions

Thin films of uniform thickness of the discussed polymers are prepared with dichloromethane. For thin film preparation, a polymer with an accurate weight is dissolved in 10 ml of dichloromethane at (25±1) °C. The above solution is heated at a temperature of 100 °C for nearly 1 h. After 1 h the solution was allowed to cool slowly to 50 °C and rapidly to 45 °C. It is formed on a flat glass slab where the solvent is allowed to evaporate at (25±1) °C. Thus a thin film of PCGH with a thickness of 100 μm is prepared. These films are kept at about room temperature for 1.0 h–2.0 h to allow most of the solvent to escape from it. Solute–solvent interaction may be easily avoided in the PAS technique. Consequently, this approach has special importance in the study of polymeric materials, as these materials are very sensitive to solute–solvent interaction. Results reveal strong absorptions in the UV region. The absorption bands in the case of PC are compared with the corresponding bands in grafted PC.

We successfully studied the optical properties of polymeric samples and their derivatives using a photoacoustic technique. It is clear from the above discussion that conventional spectroscopy is unable to characterize PMMA-G-PC co-polymers whereas the PAS technique may be efficiently used for the characterization of these co-polymers. The photoacoustic (PA) technique has a number of merits compared with other conventional methods. It has a great sensitivity and is applicable to any type of materials such as solid, semisolid, liquid, gas and transparent or opaque samples, in vacuum or in air, and to samples of any shape or size. Its other important application is the analysis of chemical reactions as well as non-radiative processes from excited state and vibrational relaxation. Our results clearly demonstrate that PAS is capable of monitoring the polymerization of pure PC into grafted polycarbonate. Thus the study of the materials like 4-aminobenzoic acid, N- [p-(carboxyl amino) acetic acid], PCPH and PCGH by this method is more suitable because this technique is very quick, requires no sample preparation and also is non-destructive.

Acknowledgement

The author acknowledges guidance and technical support from Dr. Rai A K, and Dr. Zaidi M G H in performing the experiment. The author is also grateful to Dr. Yogesh Vermani K at ITM University, Gurgaon for fruitful discussion and for reading the manuscript.

References

[1] Joshi S K, Kapil J C, Rai A K and Zaidi M G H 2003 *Physica Status Solidi* **199** 321
[2] Zaidi M G H, Shukla J S and Dixit S K 1997 *Asian J. Chemistry* **9** 583
[3] Joshi S and Rai A K 1995 *Asian J. Phys.* **5** 181
[4] Sidman J W 1958 *Chem. Rev.* **58** 689
[5] Rao C N R 1967 *Ultraviolet and Visible Spectroscopy* 2nd edn. (London: Butter Worth & Co Ltd) p. 24
[6] Rao C N R 1967 *Ultraviolet and Visible Spectroscopy* 2nd edn. (London: Butter Worth & Co Ltd) p. 65
[7] Doub L and Vandenblt J M 1947 *J. Am. Chem. Soc.* **69** 2714
[8] Gillam A E and Stern E S 1957 *Electronic Absorption Spectroscopy* (London: Edward Arnold)
[9] Sixma F L J 1964 *Manual of Physical Methods in Organic Chemistry* (New York: John Willey and Sons)
[10] Tager A 1978 *Physical Chemistry of Polymers* 2nd edn. (Moscow: Mir Publishers) Chap. 5 p. 419