Journal of Scientific Research ISSN 0555-7674
Vol. XXXVIII No. 2, December, 2008

EFFECT OF ULTRASONIC RADIATION ON POLY(VINYLCHLORIDE) AND POLYTYRENE IN SOLUTIONS

Farah Kanwal[1*], Saira Hameed [1] and Tahir Jamil[2]

[1]Institute of Chemistry, University of the Punjab, Lahore, Pakistan
[2]Faculty of Engineering and Technology, University of the Punjab, Lahore, Pakistan
*Institute of Chemistry, University of the Punjab, Lahore., Pakistan

Abstract: We are reporting the effects of ultrasonic irradiation on the degradation behavior of poly(vinylchloride) (PVC) and polystyrene (PS) in solutions. The extent of degradation was determined from the change in the average molar masses of the polymer relative to the exposure time by using viscosity method. The possibility of copolymerization of PVC and styrene was also investigated by exposing them to ultrasonic radiations in an inert atmosphere. It was concluded from the FTIR and DTA analysis that a copolymer of PVC/PS was formed by this method.

Key Words: ultrasonic, degradation, copolymerization, poly(vinyl chloride), polystyrene, styrene.

Introduction

Sonochemistry is under active investigation and has many applications in polymer and chemical processes. It has been shown that chemical reactions may be accelerated by the ultrasonic radiation. When radiation interacts with the molecules, the effect is similar to increase in temperature and can lead to a number of unexpected reactions. Ultrasonic waves can also cause depolymerisation of highly polymerized substances (such as starch, which gives dextrin) and can change the solution viscosity [1].

Most experimental investigations of polymers use ultrasonic radiation with frequency in the range 100 — 500 KHz, with the attenuation determined as a function of temperature, frequency, polymer concentration and relative molar mass. It has been shown that ultrasound treatment of poly(vinyl chloride) (PVC) solutions result in the improvement of macromolecular packing during crystallization and is attributed to the chain shortening and increase in polydispersity [2,3].

Because of partial degradation, ultrasonic treatment can lead to the formation of active radicals [4]. It was proposed that the emulsion copolymerization can be initiated for two monomers using intense ultrasonic radiation. The comonomer ratio and surfactant type can have considerable effect on the yield of copolymer [5]. Studies of polystyrene solutions have shown that the degradation process depends on the frequency of the sound wave, solvent, polymer concentration, initial molar mass and temperature [6-17]. The high intensity ultrasonic waves can induce cavitations and the shear forces created in the collapsing walls of the bubble are sufficient to produce homolytic cleavage of the polymer molecules [12]. A variety of theoretical models have been proposed to explain the effects of factors, such as frequency, intensity, solvent, temperature, nature of dissolved gas, external pressure and the molecular mass distribution on the rate and final molecular mass of degraded

1-For Proof and Correspondence: **Farah Kanwal**

species[12-17]. It was pointed out that ultrasonic degradation of polymers is distinguished from thermal degradation by scission taking place at the mid point rather than as a random event down the length of the polymer chain [18].

In this paper, we are reporting ultrasonic degradation studies of PS and PVC in solution. The degradation process is monitored as a function of radiation exposure time from the viscosity determination. We have also studied the effects of ultrasonic radiation on the copolymerization of PVC and styrene. The copolymer formation is monitored from the gain in weight of the solid material, FTIR analysis and change in glass transition temperature.

EXPERIMENTAL

Material

Poly(vinyl chloride) and polystyrene were obtained from Acros Organics, Belgium. Tetrahydrofuran (THF) from Merck was used as a solvent. Styrene monomer was obtained from Fluka. For degradation studies, Soniprep 150, ultrasonic disintegrator, Model:MSS 150.C x 3.5 was used (Sanyo Gallenkamp PLC, UK).

Ultrasonic degradation of polymers

20 ml of 1% polymer solutions of PVC and PS were sonicated in ultrasonic disintegrator. The irradiation was monitored for 200 minutes and the temperature was maintained constant at 20.0 ± 0.5 °C. During the irradiation experiment, aliquots of reaction mixture were withdrawn at 20 minutes intervals and diluted to 1% for subsequent viscosity measurements.

Ultrasonic Copolymerization

100 ml of styrene, in a separating funnel, was washed first with 5% NaOH solution and than with distilled water. The sequence of washing was repeated for three times. The styrene was distilled at 60 ^{O}C and was transferred in a flask containing molecular sieve and was placed in a refrigerator. 100 ml of filtered styrene was mixed with 100 ml of 2% PVC/THF solution. 20 ml of this styrene/PVC solution was sonicated in an ultrasonic distintegrator for 200 minute in an inert atmosphere. The sonicated solution was transferred into a 250 ml of ice cold methyl alcohol and precipitate was separated using vacuum filteration. The precipitate was vacuum dried in an oven at 50 ^{O}C for 24 hours.

Characterization

The copolymer sample was mixed with KBr powder and compressed into pellets, wherein, the copolymer powder was evenly dispersed. Fourier transform infrared spectra were recorded using Perkin Elmer A-100 spectrometer. Glass transition temperature (T_g) of all samples were measured using a DuPont differential Scanning Calorimeter model 910 with a Du Pont thermal analyzer model 9900.

RESULTS AND DISCUSSION

The degradation of PVC and PS can be monitored from viscosity measurements [19] and from the resultant average molar mass calculation. Figure 1 shows that the average molar mass of the polystyrene solution relative to exposure time. Initially, the average molar mass of PS was 2.3×10^5 g/mole. After 20 minutes of exposure time a sharp decrease in the molar mass was observed. The rate of degradation continued till 140 minutes of exposure time with the average molar mass of 2.7×10^4 g/mole and from 160 minutes of exposure time, there was no significant decrease in average molar mass.

Figure 2 shows the average molar mass of the poly(vinylchloride) solution

relative to exposure time. It is evident that a similar behavior is observed as for PS degradation. Initially, the average molar mass was 1.9 x 10^5g/mole. After 20 minutes of exposure time, a sharp decrease in the molar mass (1.3 x 10^5) was observed. The rate of degradation continued until 140 minutes of exposure time, and after 160 minutes of exposure time, there was no significant decrease in average molar mass (0.49 x 10^5g/mole) was observed. After 200 minutes of exposure time, no further degradation was observed.

Figure 3(a) shows FTIR spectrum of PS. Peaks at 907, 1025 and 1069 cm^{-1} are for C-C stretch. The peaks at 1447 cm^{-1} is for C-H bending in plane. The peak at 1598 cm^{-1} is for benzene ring, while the peaks at 2851, 2910, and 3028 cm^{-1} are for C-H stretch. FTIR spectrum (Figure 3b) of PVC shows peaks at 618 and 2914 cm^{-1} is for C-Cl stretch. The peak at 961 and 1064 cm^{-1} is for C-C stretch. The peak at 1430 cm^{-1} is for C-H bending in the plane while peaks at 2860, 2914, and 2967 cm^{-1} are for C-H stretch. Figure 3c shows the FTIR spectrum of copolymer sample-1. The peaks at 697 and 2914 cm^{-1} is for C-Cl stretch, whereas in case of PVC, the C-Cl stretch was at 618 cm^{-1}.The peak at 1446 cm^{-1} is for C-H bending in plane. Whereas in case of PS, the peak at 1447cm^{-1} is for C-H bending in plane, while in case of PVC the peak at 1430 cm^{-1} is for C-H bending in plane. The peak at 2919 cm^{-1} is for C-Cl stretch, while in case of PS the peaks at 2851, 2910 and 3028 cm^{-1} are for C-H stretch, whereas in case of PVC the C-H stretch is at 2860, and 2967 cm^{-1}. The peak at 1598 cm^{-1} is for benzene ring. The FTIR spectrum shows the formation of PVC/PS copolymer.

Table 1 shows a gain in weight of the polymer on ultrasonic radiation exposure of PVC/styrene solution. The irradiation can generate free radiels and that can lead to the formation of copolymer. From the gain in weight of the polymer, the amount of styrene in copolymer can be determined. Table 2 shows the glass transition temperature (T_g) of PS, PVC and copolymer from DTA measurements. The glass transition of PS and PVC are 75.0 and 92.0 ^{O}C respectively. A single glass transition temperature for copolymers at 81.0, 80.5, and 82.5 ^{O}C, which lie in between the T_g values of PS and PVC, is a clear evidence for the formation of PVC/PS copolymer by ultrasonic radiation.

CONCLUSION

It can be concluded from the experimental results that the solutions of poly(vinyl chloride) and polystyrene degrade when exposed to ultrasonic radiations. The degradation rate was very rapid at 20 min. After irradiation for 200 min, no further degradation was observed. Due to the ultrasonic degradation of PVC/styrene solution, active PVC and styrene radicals are generated and produce new PVC/PS copolymer product. FTIR and DTA analysis confirms the formation of copolymer.

ACKNOWLEDGEMENT

We wish to thank department of chemistry, GCU, Lahore, Pakistan, for the use of facilities and assistance in the synthesis of the copolymer and FTIR analysis. We also like to thank PCSIR laboratory staff for assistance in DTA measurements.

References

1. Mason, J. T., Lorimer, P. J., Sonochemistry (Theory, Applications and the use of ultrasound in Chemistry), John Wiley & Sons, 1998.
2. Walton, D. J., Mason, T. J., Synth.Org.Sonochem.1998, 263-300.
3. Lorimer, J. P., Mason, T. J., Ultrasonochem. 1995, 2, 79-S86.
4. Ngugen, T. Q., Liang, Qi.Z. Kaush, H. H., Polymer.1997, 38(15), 3785-3793.
5. Jiang, L., Keqiang, C., Zhili, L., Polym. J.(Tokyo).32, 2,103-106.
6. Glynn, P. A., Van der Hoff, B. M. J., Macromol. Sci 1973; A7:1965.
7. Driscoll, K. F., Sridharn, A. U., J. Polym. Chem.Ed.1973; 11; 1111.
8. Mostafa, M. A., J. Polym. Sci.1958; 33:295.
9. Thomas, B. B., Alexander, W. J., J. Polym. Sci.1957; 25:285.
10. Brett, H. W. W., Jellinek, H. H. G., J. Polym.Sci.1954, 13441.
11. Schmid, G., Rommel, O. Z., Phys. Chem.1939, A185, 97-659.
12. Price, G. J., Smith, P. F., Polymer.1993, 34, 4111-7.
13. Weissler, A., J. Appl. Phys.1950, 21, 171.
14. Jellinek, H. H. G., Brett, H. W., J. Polym. Sci.1954, 13, 111.
15. Doulah, M. S., J. Appl. Polym. Sci.1978, 22, 1735.
16. Glyn, P. A. R., Vander Hoff, B. M. J., Reilly, P. M., J. Macromol. Sci. Chem.1972, A6 (8), 1653.
17. Kanwal, F., Liggat, J. J., Petrick, R. A., Polym. Degrad. Stab.2000, 68, 445-9.
18. Madras, G., McCoy, B. J., AICHE Journal, 2001, 47, 2341-8. Mee, J. A., Wheeler, S. M. D., Physical Chemistry, p-661, William Heinemann, Ltd. London. XIX

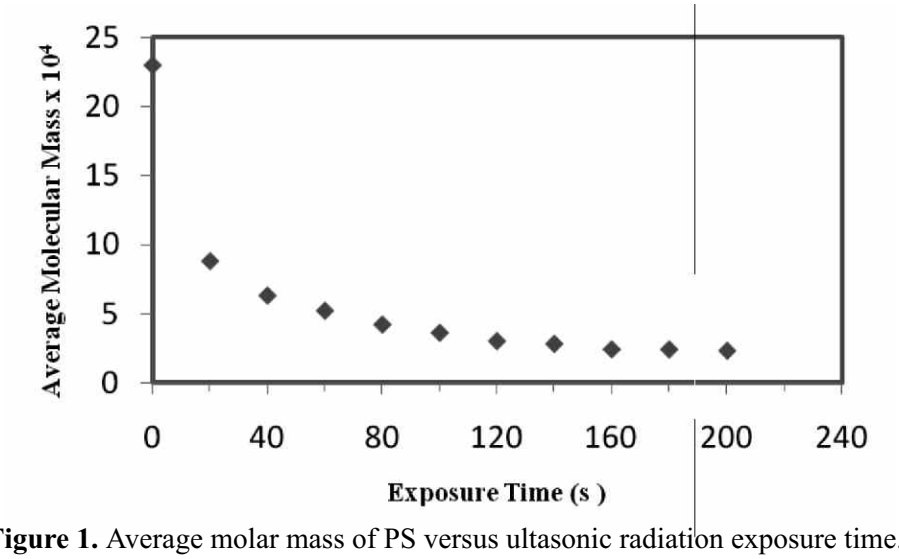

Figure 1. Average molar mass of PS versus ultasonic radiation exposure time.

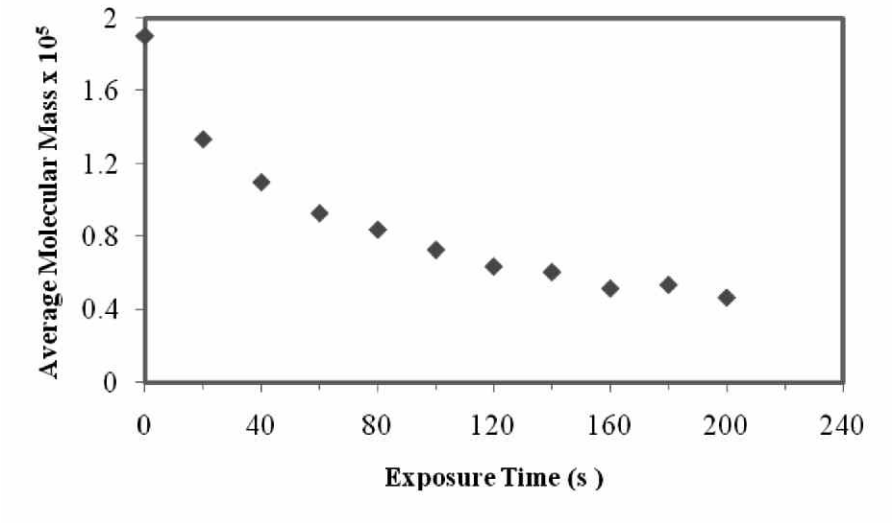

Figure 2. Average molar mass of PVC versus ultasonic radiation exposure time.

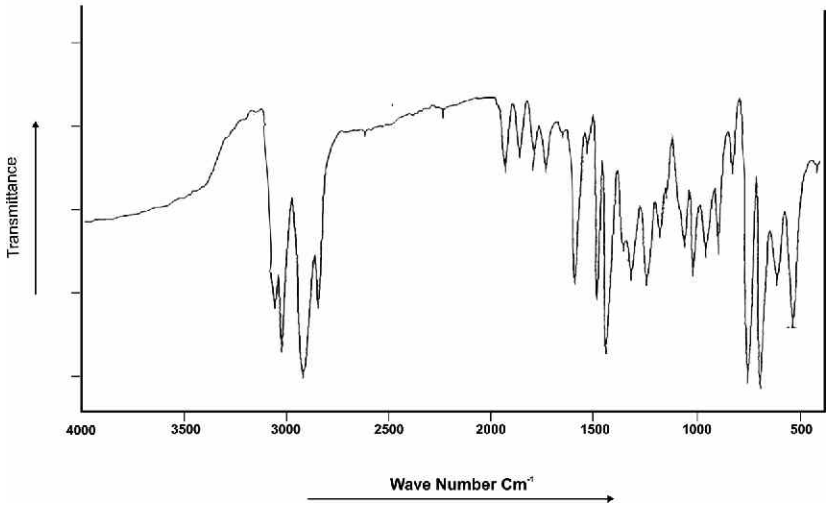

Figure 3a. FTIR spectra of polystyrene.

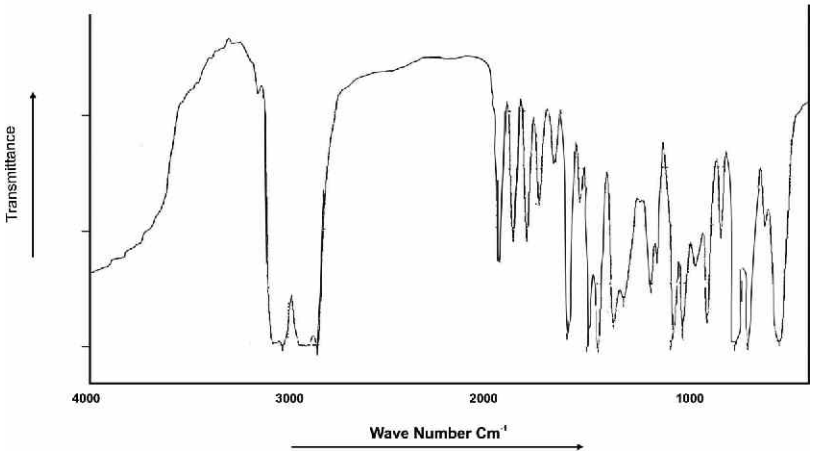

Figure 3b. FTIR spectra of poly(vinylchloride).

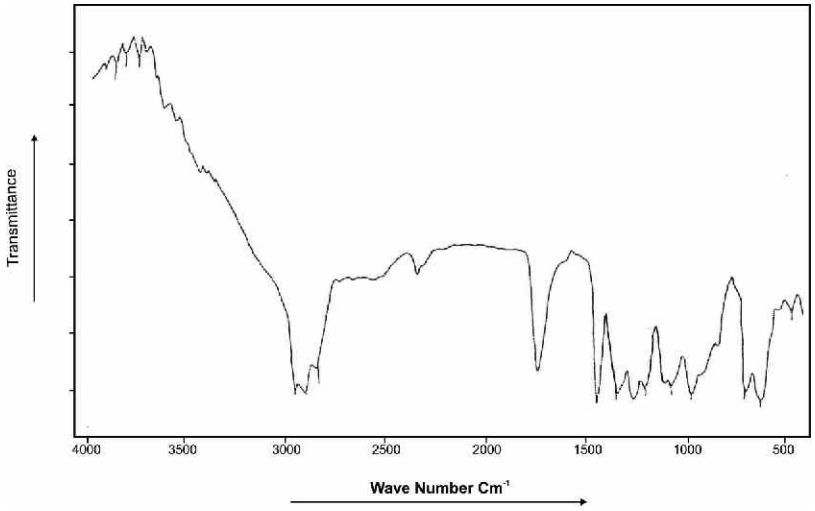

Figure 3c. FTIR spectra of PVC/PS copolymer.

Sample:	PVC in styrene (gm)	Copolymer (gm)	Weight gain (%)
PVC/PS copolymer-1	2.0	2.2	10
PVC/PS copolymer-2	2.0	2.48	24
PVC/PS copolymer-3	2.0	2.16	8

Table 1. Weight gain (%) of copolymers. All the copolymers were synthesized under the same reaction conditions.

Sample	T_g (^OC)
Polystyrene (PS)	75.0
Poly(vinylchloride) (PVC)	92.0
PVC/PS copolymer-1	81.0
PVC/PS copolymer-2	80.5
PVC/PS copolymer-3	82.5

Table 2. Glass transition temperature (T_g) of copolymers from DTA measurements.