CHAPTER III

3.1 Experimental

3.1.1 Materials used

Methyl acrylate and styrene were purchased from Merck India Ltd. Solvents like tetrahydrofuran (THF), 1, 4-dioxane, and toluene were procured from S.D. Fine Chem., India Ltd. and benzoyl peroxide (BZP) from LOBA Chemicals. Base oils were collected from Indian Oil Corporation Ltd., Dhakuria, Kolkata.

3.1.2 Purification of the materials

Methyl acrylate (MA) was shaken two to three times with 5% sodium hydroxide to eliminate hydroquinone inhibitor, dried over anhydrous $CaCl_2$ for 7-8 h and distilled. Benzoyl peroxide (BZP) was used as initiator after recrystaliztion from $CHCl_3$-MeOH mixture, THF, 1, 4-Dioxane, and toluene were purified by distillation after being refluxed for 2 h in presence of sodium.

3.1.3 Polymerization

The copolymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel to add styrene drop wise. In the flask was placed desired mass of MA and initiator (BZP) followed by the desired mass of styrene, added drop wise for 2 h in the presence of different solvents (toluene, tetrahydrofuran and 1, 4-dioxane). The reaction temperature was maintained at 353K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313K. A homopolymer of MA was similarly prepared and purified under the same conditions for use in reference experiments.

3.1.4 Spectroscopic Measurements

IR spectra were recorded on a Shimudzu FT-IR 8300 Spectrometer using 0.1 mm KBr cells and the spectra were recorded at room temperature within the wave number range 400 to 4000 cm^{-1}. NMR spectra were recorded in Brucker Avance 300 MHz FT-NMR Spectrophotometer using 5 mm BBO probe. $CDCl_3$ was used as solvent and TMS as reference material.

3.1.5 Viscometric measurements.

Viscometric properties were determined at 303 K, 313 K and 323 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values, $K' = 0.00268\ cm^2\ sec^{-2}$, $L = -19.83\ cm^2$ and volume of the bulb is 3 cm^3 and length of the capillary 11.3 cm). Experimental determination was carried out by counting time flow for at least seven different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and uncertainty was found to be nearly 0.17 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants $K = 0.00387\ dl.g^{-1}$ and $a = 0.725$ [37, 38] were employed.

3.1.6 Evaluation of prepared polymer as pour point depressant in base oils

The prepared additives were evaluated as pour point depressant using base oils (B1 and B2) collected from two different sources (S1 and S2), through the pour point test according to the ASTM–D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentrations were 0.25%, 0.50%, 1%, 2%, 3% and 5 % (w/w). The experimental data were noted by taking an average of three experimental results under identical conditions.

3.1.7 Evaluation of prepared polymer as viscosity index improvers in base oils

The various blends were prepared by using two different types of base stocks (B1 and B2). Viscosity index of these oils were calculated by ASTM D 2270-87 method using viscosity index calculator. The kinematic viscosities of the polymer doped base oils were determined at 40^0C and 100^0C. Range of concentration of the additives (in lube oils) used to study the effect of concentration on VI of the lube oil, were 0.25%, 0.50%, 1%, 2%, 3% and 5 % (w/w).

3.2 References

[1] Akhmedov, A. I.; Copolymers of alkyl methacrylates with styrene as V. I. improvers for lubricating oils, *Chem. Technol-Fuels-Oils*, **1987**, 23(3–4), 147–151.

[2] Eckert, R. J. A.; Wortel, J. M.; Hydroxy-functional acrylic copolymers, Shell Oil, *US Patent 3,642,633*, February 15, **1972**.

[3] Ford, J. F.; Wood, I. M.; Phosphoramidates of Alpha-olefin Polymers, The British Petroleum Co. Limited, *US Patent 3,562,16*, February 9, **1971**.

[4] Kapur, G. S.; Sarpal, A. S.; Mazumdar, S. K.; Jain, S. K.; Srivastava, S. P.; Bhatnagar, A. K.; Structure—performance relationships of viscosity index improvers: I microstructural determination of olefin copolymers by NMR spectroscopy, *Lubrication Science*, **1995**, 8(1), 49–60.

[5] Mohamed, M. M.; Hamdi, H. A.; Mohamed, F. E. J.; Multi- functional viscosity improvers, *Chem. Tech. Biotechnol*, **1994**, 60, 283–289.

[6] Schwab, F. C.; Heilweil, I. J.; Styrene-alkylene oxide block Copolymers, Mobil Oil Corporation, *US Patent 3,954,91*, May 4, **1976**.

[7] Ranney, M. W.; Lubricant Additives, *New Jersey: Noyes Data Corporation*, 1978.

[8] Dean, E. W.; Baner, A. D.; Berglund, J. H.: Vicosity index of lubricating oils, *Ind. Eng. Chem.*, **1940**, 32:102.

[9] Eckert, R. J. A.; Covey, D. F.; Developments in the field of hydrogenated diene copolymer as viscosity index improvers, 5th International Colloquium, *Technishe Akademie, Esslingen*, **1986**.

[10] Abdel-Azim, A. A. A.; Huglin, M. B.; Second proceedings of the conference of chemical engineering, Cairo, Egypt, **1984a**, March18-20, pp. 111–116.

[11] Abdel-Azim, A.; Huglin, M. B.; Selective solvation of polystyrene in tetralin/cyclohexane mixtures, *Polymer*, **1983**, 24, 1308-1312.

[12] Abdel-Azim, A. A. A.; Huglin,M. B.; Proceedings of the second egyptian conference of chemical engineering, Cairo, Egypt, **1984b**, March 18-20, pp.117-123.

[13] Nehal, S. A.; Ph.D. Thesis, *Ain Shams University*, Cairo, Egypt, **1996**.

[14] Eckert, R.J.A.; Covey, D.F.; Developments in the field of hydrogenated diene copolymers as viscosity index improvers, *Lubr. Sci.*, **1988**, 1, 65–80.

[15] Pirro, D. M.; Wessol, A. A.; *Lubrication Fundamentals*, New York: Marcel Dekker, **2001**, pp. 37–43.

[16] Graulin, G.; Swire, E. A.; Jones, S. P.; Pour point depression of lubricating oils, *Ind. Eng. Chem.*, **1953**, 45(10), 2327-2335.

[17] Srivastava, S. P.; Tandon, R. S.; Verma, P.S ; Saxena, A. K.; Joshi, G. C.; Phatak, S. D.; Crystalyzation behaviour of n-paraffins in Bombay-high middle-distillate wax/gel, *Fuel*, **1992**, 71, 533-537.

[18] Zuo, J. Y.; Zhang, D. D.; Ng, H. J.; An improved thermodyanamic model for wax precipitation from petroleum fluids, *Chem. Eng. Sci.*, **2001**, 56, 6941-6947.

[19] Handoo, J.; Srivastava, S. P.; Agrawal, K. M.; Joshi, G. C.; Thermal properties of some petroleum waxes in relation to their composition, *Fuel*, 68(10), **1989**, 1346-1348.

[20] Coutinho, J. A. P.; Cauphin, C.; Daridon, J. L.; Measurements and modelling of wax formation in diesel fuels, *Fuel*, **2000**, 79(6), 607-616.

[21] Holder, G. A.; Winkler, J.; *Nature*, **1965**, 207, 719-722.

[22] El-Gamal, I. M.; Al-Sabbagh, A. M., Polymeric additives for improving the flow properties of waxy distillate fuels and crudes, *Fuel*, **1996**, 75(6), 743-750.

[23] Lorensen, L. E.; American Chemical Society Meeting, *Petroleum Division*, **1962**, Sept. 9-14, Preprints 7 (4-B), B61.

[24] Amal, M. N.; Preparation and evaluation of some polymeric compounds as lube oil additives., *J. Faculty Edu.*, **2001**, 26, 309–321.

[25] Denis, J.; Pour point depressants in lubricating oils, *Lubr. Sci.*, 1(2), 103–129.

[26] Florea, M.; Catrinoiu, D.; Luca, P.; Balliu, S.; The influence of chemical composition on the pour-point depressant properties of methacrylate copolymers used as additives for lubricating oils, *Lubr. Sci.* **1999**, 12(1), 31–44.

[27] Anwar, M.; Khan, H.; Nautiyal, S.; Agrawal, K. M.; Rawat, B. S.; Solubilised waxes and their influence on flow properties of lube oil base stocks, *Pet. Sci. Technol.*, **1999**, 17(5-6), 491–501.

[28] Bruson, H. A.; "Process for preparing esters and products", *Rohm and Hass co., U.S. Patent 2,100,993*, Dec. 14. **1934**.

[29] Abdel Azim, A. A.; Amal, M. N.; Nehal, S. A.; Rasha, S. K.; El Nagdy, E. I.; Preparation and evaluation of acrylate polymers as viscosity index improves for lube oil, *Pet. Sci. and Tech.*, 2005, 23, 537–546.

[30] Khidir, T. T.; Synthesis and evaluation of copolymers as pour point Depressant, *Pet. Sci. and Tech.*, **2007**, 25, 671-681.

[31] Florea, M.; Catrinoiu D.; Lucca P.; Balliu S ; The influence of chemical composition on the pour point depressant properties of methacrylate copolymers used as additive for lubricating oils. *Lubrication Science*, **1999**, 12-1, 31-44.

[32] Abdel-Azim, A.; Amal, M. N.; Nehal, S. A.; Rasha, S. K.; Preparation and evaluation of acrylate polymers as pour point depressants for lube oil, *Pet Sci. Tech.*, **2006**, 24, 887- 894.

[33] Nassar, A. M.; Synthesis and evaluation of viscosity index improvers and pour point depressant for lube oil, *Pet. Sci. and Tech.*, **2008,** 26, 523-531.

[34] Ghosh, P.; Pantar, A.V.; Sarma, A. S.; Alkyl Methacrylate : α-Olefin copolymers as viscosity modifier additives in lubricants, *Ind. J. Chem. Tech.*, **1998**, 5, 371-375.

[35] Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kafrawy, A. F. E. I.; Kamal, R S.; *Pet. Sci. and Tech.*, **2009**, 27, 20-32.

[36] Delpech, M. C.; Oliveira, C. M. F.; Viscometric study of poly (methyl methacrylate -g-propylene oxide) and respective homopolymers, *Polym. Test*, **2005**, 24, 381.

[37] Ivana, I mello; Delpech, M. C.; Coutinho, F. M. B.; Albino F. F. M.; Viscometric study of high-cispolybutadiene in toluene solution, *J. Braz Chem Soc.*, **2006**, 17(1).

[38] Ghosh, P.; Das, T.; Nandi, D. Synthsis of copolymers and homopolymers of methyl methacrylate and styrene and studies on their viscometric properties in three different solvents, *Research journal of chemistry and environment*, **2009**, 13(1), 17-25.

[39] Abdel-Azim A. A. A.; Atta, A. M.; Farahat; M. S.; Boutros, W. Y.; Determination of intrinsic viscosity of polymeric compounds through a single specific viscosity determination, *Polymer*, **1998**, 39, 26.

[40] Tager, A.; Physical chemistry of polymers, *Mir Publishers*, Moscow. **1972**

[41] Oliveira, C. M. F.; Andrade, C. T.; Delpech, M. C.; Properties of poly (methyl methacrylate-g-propylene oxide) in solution, *Polym. Bull.*, **1991**, 26, 657.

[42] Delpech, M. C., Coutinho, F. M. B., Habibe, M. E. S., Viscometry study of ethylene-cyclic olefin copolymers, *Polym. Test.*, **2002**, 21, 411.

[43] Schoff, C. K.; Concentration dependence of the viscosity of dilute polymer solutions: Huggins and Schulz-Blaschke constants, *Polymer Handbook*, *John Wiley*: New York, **1999**

[45] Bataille, P.; Sharifi-sajani, N.; Evin, E.; Preparation and characterization of a viscosity index improver for naphthenic and paraffinic Base oils, *Journal of solution chemistry*, **1994**, 23, 2.

[46] Abdel-Azim, A. A. A.; Nasser, A. M.; Ahmed, N. S.; Ka frawy, A. F. F. I.; Kamal, R. S.; Multifunctional additives viscosity index improvers, pour point depressants and dispersants for lube oil, *Pet. Sci. and Tech.*, **2009**, 27, 20-32.

[47] Nassar, A. M.; Ahmed, N.S.; Study the influence of some polymeric additives as viscosity index improvers, pour point depressants and dispersants for lube oil, *Pet. Sci. and Tech.*, **2010**, 28, 13–26.

[44] Delpech, M. C.; Coutinho, F. M. B.; Habibe, M. E. S.; Bisphenol A-based polycarbonates: characterization of commercial samples, *Polym. Test.*, **2002**, 21(2), 155-161.