

## CHAPTER III

### 3.1 Experimental

#### 3.1.1 Materials used

Acrylic acid (GC Purity 99%), procured from Thomas Baker, India, decyl alcohol (GC Purity 98%), obtained from S. D. Fine Chemicals Ltd, India, styrene obtained from Merck Products, Germany and hydroquinone procured from S. D. Fine Chemicals Ltd, India, were used. Benzoyl peroxide (GC Purity 98%), procured from Loba Chemicals Pvt. Ltd., India, and was purified by crystallization from methanol-chloroform mixture prior to use. Toluene (GC Purity 99.5 %) and chloroform (GC Purity 99 %), obtained from Merck, India, were used as a solvent.

#### 3.1.2. Esterification of decyl acrylate (DA) from acrylic acid and decyl alcohol

Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1:1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of catalytic amount of concentrated sulphuric acid, 0.25% hydroquinone (with respect to the monomer) as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403K using a well-controlled thermostat. The progress of the reaction was followed by monitoring the amount of liberated water from the reaction mixture to give the ester, decyl acrylate.

#### 3.1.3. Purification of the prepared ester

The prepared ester was purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h, and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide, the ester was then left overnight on calcium chloride and was then removed by distillation under reduced

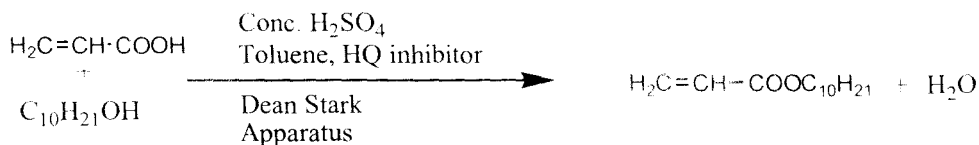
pressure and was used in the polymerization process.

#### **3.1.4. Preparation of homopolymer of DA and its copolymer with styrene and their purification**

The polymerization 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 DA and initiator (BZP) followed by the desired mass of styrene was added dropwise for 2 h in the presence of toluene as solvent. 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 to 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 DA was similarly prepared and purified under the same conditions for use in reference experiments.

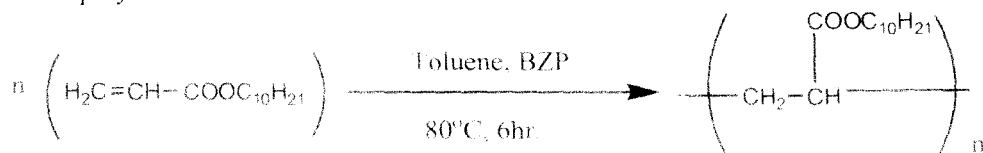
### Scheme I

Esterification:



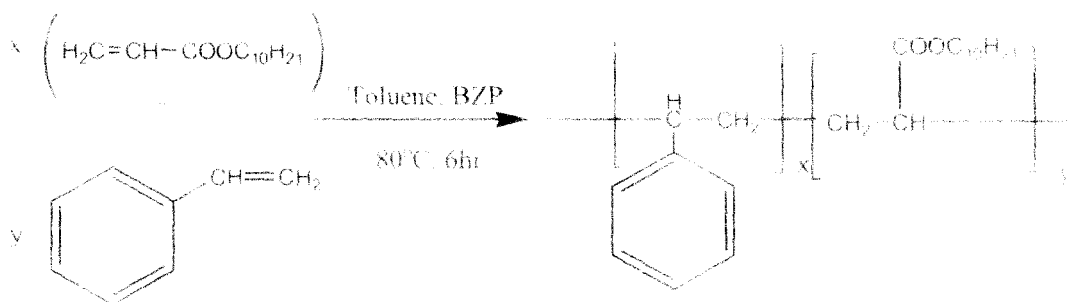
### Scheme-II

Homopolymerisation:



### Scheme-III

Copolymerisation:



## 3.1.5. Spectroscopic Measurements

IR spectra were recorded on a Shimadzu 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  $\text{cm}^{-1}$ . NMR spectra were recorded in a Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe.  $\text{CDCl}_3$  was used as solvent and TMS as reference material.

## 3.1.6. Viscometric Measurements

Viscosities were determined at 313K in chloroform and toluene, using an Ubbelohde OB viscometer placed in a thermostatically controlled bath. The temperature was measured close to the capillary by a thermometer with an accuracy of

0.01K. Experimental determination was carried out by counting time flow at least six 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 the solvent were taken in all the cases.

All the binary solutions were prepared by dissolving a measured weight of the polymer in chloroform and toluene and diluting to a measured volume. All the ternary solutions were prepared by dissolving a measured weight of the polymers with a DA : copolymer of DA with styrene weight ratio of 3:1, 1:1 and 1:3 in chloroform and toluene and then diluting to a measured volume.

For the viscosity – average molecular weight determination, the constants  $K = 0.00387 \text{ dl/g}$  and  $a = 0.725$  [41, 46] were employed in toluene and the constants  $K = 0.00480 \text{ dl/g}$  and  $a = 0.80$  [47] were employed in chloroform.

### **3.1.7. Evaluation of prepared additive as pour point depressants (PPDs) in base oils**

The prepared additives were evaluated as pour point depressant using two different base oils collected from the same source, (**Table 5**) 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 concentration for individual polymers (binary) and polymer blends (ternary). All the ternary blend solutions were prepared by dissolving a measured weight of the polymers with DA: copolymer of DA with styrene at the weight ratio of 3:1, 1:1 and 1:3 in base oils. The effect of additive concentration was investigated by using different doping concentrations from 0.25% to 3% (w/w). The experimental data were noted by taking an average of three experimental results under identical conditions.

### 3.1.8. Evaluation of prepared additive as viscosity index improvers (VIIs) in base oils

Different binary and ternary blends were prepared by using two different types of base oil. Viscosities and the viscosity index (VI) of these oils were calculated according to ASTM D2270. Different weight percentages of concentration from 0.25 to 3.0 were used to study the effect of concentration on VI of the additive-doped lube oil. The experiment was done for both binary and ternary blends. In this respect, the kinematic viscosity of the oil containing different concentrations of the prepared polymers, copolymers and polymer blends were determined at 313K and 373K. The experimental data were noted by taking an average of three experimental results under identical conditions.

### 3.2. References

- [1] Leisen, P. J.; Jao, C. T.; Li, S.; (Meth)Acrylate copolymer pour point depressants, *U. S. Patent No. 6,255,261*, **2001**
- [2] El-Ghazawy, A. R.; Farag, K. R.; Synthesis and characterization of novel pour point depressants based on maleic anhydride-alkyl acrylates terpolymers, *J. App. Polym. Sci.*, **2010**, 115, 72–78.
- [3] Abdel-Azim, A. A. 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.
- [4] Jukić, A.; Tomašek, L. J.; Janović, Z.; Polyolefin and poly(alkyl methacrylate) mixed additives as mineral lubricating oil rheology modifiers, *Lub. Sci.*, **2005**, 17, 431-449.
- [5] Mortier R. M.; Qrszulik S. T.; Chemistry and Technology of Lubricants, *Blackie Academic and Profession*, London, **1997**.

- [6] Gallucci, R. R.; Mullen, T.; Odle, R.; Sheth, C. K.; White, M. J.; Methods of making polymer blends compositions, *U. S. Patent No. 8,268,934 B2*, **2012**.
- [7] Ghosh, P.; Pantar, A. V.; Sarma, A. S.; Alkyl methacrylate:  $\alpha$ -olefin copolymers as viscosity modifier additives in lubricants, *Indian J. Chem. Technol.*, **1998**, 5, 371-375
- [8] Yang, H.; Zhu, P. P.; Wang, S. Q.; Guo, Q. P.; Viscometric study of polymer-polymer interactions in ternary systems-I. Viscometric behavior in compatible polymers in solution, *Eur. Polym. J.*, **1998**, 34(3-4), 463-467
- [9] Kulshreshtha, A. K.; Singh, B. P.; Sharma, Y. N.; Viscometric determination of compatibility in PVC/ABS polyblends-II. Reduced viscosity-concentration plots. *Eur. Polym. J.*, **1988**, 24, 33-35.
- [10] Hugelin, P. C.; Dondos, A.; Ternary systems: A polymer/polymer B/solvent. influence of the nature of the solvent on the incompatibility of polymers, *Macromolecular Chem.*, **1969**, 126, 206-216.
- [11] Huang, C.; Viscosity improver compositions providing low characteristics to lubricating oil. *U.S. Patent 7 402 235 B2*, Jul. 22, **2008**.
- [12] Canich, M. J. A.; Datta, S.; Farnig, O. L.; Kolb, R.; Bernero, V. M.; Sirota, B. E.; Sun, T. T.; Tre, F. M.; V-Nair, M.; Polymeric compositions useful as rheology modifiers and methods for making such compositions, *E. Patent 2424939 A1*, Mar. 7, **2012**.
- [13] Biggs, T. R.; Jung, K. A.; Kapuscinski, M. M.; Moore, W. J.; Polymer blends containing olefin copolymers and star branched polymers, *E. Patent 0794995 A1*, Sep. 17, **1997**.

- [14] Gravlin, G.; Swire, E. A.; and Jones, S. P.; Pour point depression of lubricating oil. *Ind. Eng. Chem.*, **1953**, 45, 2327.
- [15] Lorensen, L. E.: *Am. Chem. Soc. Meeting*, Sept. 9–14, Petroleum Div Preprints, **1962**, 7(4-B):B61.
- [16] Amal, M. N.: Preparation and evaluation of some polymeric compounds as lube oil additives. *J. Faculty Edu.*, **2001**, 26, 309–321.
- [17] Al-Sabagh, A. M., Noor, El-Din M. R.; Morsi, R. E.; Elsabee M. Z., Oil soluble styrene-maleic anhydride copolymer derivatives and their flow improver properties of waxy crude oil, *J. Pet. Sc. and Eng* **2009**, 65, 139-46.
- [18] Amal, M. N., Nehal S. A., Rasha, S. K., Abdel-Azim, A. A. A., El-Nagdy, E. I.: Preparation and evaluation of acrylate polymers as viscosity index improvers for lube oil, *Pet. Sci. Tech.*, **2005**, 23, 537–546.
- [19] Nassar, A. M., Ahmed, N. S., Synthesis and evaluation of ethoxylated polyesters as viscosity index improvers and pour point depressants for lube oil, *Intl. J. Polymeric Mater.*, **2003**, 52, 821–832.
- [20] Huggins, M. L.: The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. *J. Am. Chem. Soc.* **1942**, 64, 2716.
- [21] Krigbaum, W.; Wall, F. J.; Viscosities of binary polymeric mixtures, *J. Polym. Sci.*, **1950**, 5, 505.
- [22] Williamson, G. R.; Wright, B.; Interactions in binary polymer systems, *J. Polym. Sci. Part A*, **1965**, A3, 3885.
- [23] Garcia, R.; Melad, O.; Gomez, C. M.; Figueruelo, J. E.; Campos, A.;

- Viscometric study on the compatibility of polymer-polymer mixtures in solution, *Eur. Polym. J.*, **1999**, 35, 47-55.
- [24] Sun, Z.; Wang, W.; Feng, Z.; Criterion of polymer-polymer miscibility determined by viscometry, *Eur. Polym. J.*, **1992**, 28, 125.
- [25] Yang, H.; Zhu, P. P.; Wang, S. Q.; Zeng, Y. M.; Guo, Q. P.; Viscometric study of polymer-polymer interactions in ternary systems—II The influence of solvent. *Eur. Polym. J.* **1998**, 34, 9, 1303-1308.
- [26] Ghosh, P.; Das, T.; Nandi, D.; Karamakar, G.; Mandal, A., Synthesis and lubricating characterization Of biodegradable polymer – used as pour point depressant for Oil, *Int. J. Polym. Mater.*, **2011**, 59, 1008–1017.
- [27] Selvakumar, M.; Bhat, D. K.; Renganathan N. G.; Miscibility of polymethylmethacrylate and poly ethyl eneglycol blends in tetrahydrofuran, *J. App. Polym. Sci.*, **2009**, 111, 452-460.
- [28] Paul, D. R.; Newman, S.; Eds. Polymer Blends, *academic Press: New York, Vols. 1 and 2*, **1978**.
- [29] Brandrup, J.; Immergut, E. H.; Grulke, E. A.: Polymer Handbook; *New York: Wiley Interscience*, **1999**.
- [30] Coleman, M. M.; Graf, J. F.; Paiter, P. C.: Specific Interactions and the miscibility ...of polymer blends., *Lancaster: Technomic*, **1991**.
- [31] Varnell, D. F.; Runt, J. P.; Coleman, M. M.; *FT i.r. and thermal analysis studies of blends of poly( $\epsilon$ -caprolactone) with homo- and copolymers of poly(vinylidene chloride)*, *Polymer*, **1983**, 24, 37-42.
- [32] Abdel-Azim, A. A. A.; Nasser, A. M.; Ahmed, N. S.; Kafrawy, A. F. E. I.; Kamal, R.S.; Multifunctional additives viscosity index improvers, Pour point depressants and dispersants for lube oil, *Petroleum Science*



*and Technology*, **2009**, 27, 20-32.

- [33] 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, *Petroleum Science and Technology*, **2010**, 28, 13–26.
- [34] Manson, J. A.; Sperling, L. H.; Polymer Blends and Composites, *Plenum Press, New York*, **1978**.
- [35] Bucknall, C. B.; Toughened Plastics, *Appl. Sci. Publ., London*, **1977**.
- [36] Walsh, D. J.; Higgins, J. S.; Macconnachie (Eds.),A.. Polymer Blends and Mixtures, *Martinus Nijhoff, Dordrecht*, **1986**.
- [37] Utracki, L. A.; Weiss (Eds.), R. A.; Multiphase polymers—blends and ionomers, ACS Symp. Ser. 395, *American Chemical Society, Washington, DC*, **1989**.
- [38] Olabisi, O., Robeson, L. M.; Shaw, M. T.; Polymer-polymer miscibility, *Academic Press, New York*, **1979**.
- [39] Vukovi, E. R.; Karasz, F. E.; MacKnight, W. J.; *Polymer*, **1983**, 24, 529.
- [40] Ghosh, P., Das, U. Nandi, D.; Synthesis 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.
- [41] 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.
- [42] Delpech, M. C.; Coutinho, F. M. B.; Habibe, M. E. S.; Viscometry study

of ethylene-cyclic olefin copolymers, *Polym. Test.*, **2002**, 21(4), 411-415.

- [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**.
- [44] 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.
- [45] Khan, H. U., Gupta, V. K., Bhargava, G. S.; Determination of intrinsic viscosity of high polymers through a single specific viscosity measurements, *Commun.*, **1983**, 24, 191.
- [46] Srivastava, D.; Development of mesophormic poly(methylmethacrylate). *Iranian Polym. J.* **2003**, 12(6), 449.
- [47] Wagner, L. H.; The Mark-Houwink-Sakurada relation for (methyl methacrylate), *J. Phys. Chem.*, **1987**, 16 (2).

