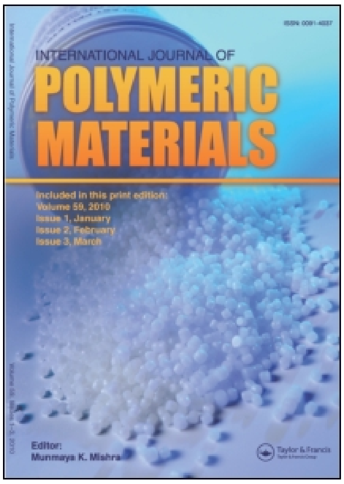

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and evaluation of ethoxylated polyesters as viscosity index improvers and pour point depressants for lube oil

Amal M. Nassar[a]; Nehal S. Ahmed[a]
[a] Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr city, Cairo, Egypt

To cite this Article Nassar, Amal M. and Ahmed, Nehal S.(2003) 'Synthesis and evaluation of ethoxylated polyesters as viscosity index improvers and pour point depressants for lube oil', International Journal of Polymeric Materials, 52: 9, 821 — 832

To link to this Article: DOI: 10.1080/713743712

URL: http://dx.doi.org/10.1080/713743712

International Journal of Polymeric Materials, 52:821–832, 2003

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390231861

SYNTHESIS AND EVALUATION OF ETHOXYLATED POLYESTERS AS VISCOSITY INDEX IMPROVERS AND POUR POINT DEPRESSANTS FOR LUBE OIL

Amal M. Nassar
Nehal S. Ahmed
Department of Petroleum Applications,
Egyptian Petroleum Research Institute,
Nasr city, Cairo, Egypt

This work is confined to the preparation and characterization of two sets of copolymeric additives. The first set is based on poly(propylene sebacate), while the second set is based on poly(propylene succinate). These two polymeric polyesters were ethoxylated with two different molecular weights of poly(ethylene glycol) (M. Wt. 400 and 600) to prepare four additives. The molecular weights of the prepared polyesters were determined by GPC. The efficiency of the prepared copolymers for improving the viscosity index and lowering the pour point of the base lube oil was studied. It was found that the efficiency increases with increased molecular weight of the prepared copolymers.

Keywords: lube oil additives, viscosity index improvers, pour point depressants, copolymers

INTRODUCTION

Lubricating oil always contains different types of additives. These additives differ in quantity and quality according to the purpose for which they are needed. Lubricant additives are compounds or mixtures when incorporated in base lubricating fluids, supplement their natural characteristics and improve their field service performance in existing applications. Lube oil additives may be classified as: detergents, dispersants, antioxidants, corrosion inhibitors, extreme pressure agents, viscosity index improvers, and pour point depressants [1–7]. The viscosity index (VI) expresses the viscosity changes of

Received 2 April 2001; in final form 7 May 2001.

Address correspondence to N. S. Ahmed, Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, 11727, Cairo, Egypt.

an oil when temperature is varied, [8] i.e., the smaller changes of the viscosity named as the higher viscosity index. As a rule the VI of lubricating oils obtained from mineral oils according to conventional processes is not sufficiently high for satisfying the very severe specifications relating to viscosity that are required by the modern engines. Various compounds, generally polymeric ones, have already been proposed [9–16] as additives for lubricating oils. The polymer molecule in solution exists as a random coil that is swollen by the solvent [17, 18]. The volume of this molecule determines the viscosity increase as a function of solvation power, which is related to the temperature [19–23]. The polymeric additive dissolved in the lube oil resembles a tangled ball in which some of the solvent (lube oil) molecules are incorporated, forming a micelle. As the temperature is raised the lube oil viscosity decreases; meanwhile, the polymer molecule expands, due to the increase in the solvating power, and hence the size of the micelle increases. The increase in the micelle size counterbalances the reduction of the viscosity of the lube oil and hence reduces the changes of viscosity with temperature of the mixture. Consequently, the performance of the viscosity index improver depends on the behavior of the polymer molecules in the oil where the polymer solubility, molecular weight, and resistance to shear degradation are determinant parameters [24].

The pour point of lubricating oil is the lowest temperature, expressed as multiple of 5°F (or 3°C), at which the oil stays flowing. Most oils contain some dissolved wax, which begins to separate as crystals that interlock to form a rigid structure, which traps the oil in small pockets. Such wax crystals formed in lubricating oils assume [25] a lattice–like structure that traps the liquid oil and keep it from pouring or flowing. Low pour point may be achieved by intensively dewaxing the oil during refining. However, the deep dewaxing of oil fractions decreases its oxidation stability and increases the tendency toward carbon deposits. Thus, to lower the pour point of oils still containing even small amounts of paraffin and resin, it has been suggested that it is more logical to add a pour point depressant [26–29]. Many compounds were used as pour point depressants for waxy petroleum fractions [30, 31], but only two classes have achieved commercial success. The first is alkylated naphthalenes prepared from wax chlorides, while the second class includes a variety of high molecular weight polymeric compounds.

The present work aims to synthesis two sets of polymeric additives to be used as viscosity index improvers and pour point depressants. The first set is based on ethoxylated poly(propylene sebacate) while the second set is based on ethoxylated poly(propylene succinate). The ethoxylation of the synthesized polyesters is attained by reaction with two different molecular weights of poly(ethylene glycol) (400 and 600). The second aim of this investigation is to evaluate the efficiency of the prepared ethoxylated copolymers as viscosity index improvers and pour point depressants.

EXPERIMENTAL

1. Preparation of the Polyesters

1.1 mole of propylene glycol was charged in a four-necked flask and heated until 80°C was reached with nitrogen flushing and continuous stirring. 1 mole of succinic or sebacic acid was added. The temperature was raised to 150°C over a period of 3 h, then raised to 190°C over a period of 4 h. The temperature was kept constant at 190°C to 200°C for 1 h. Then the temperature was lowered to 170°C until the acid value became zero. Two polyesters were obtained. The first was propylene succinate (A), and the second was propylene sebacate (B).

2. Ethoxylation of Polyesters [32]

0.2 mole of 2,2′-dichloro diethyl ether, 0.1 mole polyester A or B, 0.2 mole NaOH and 0.5 mole poly(ethylene glycol) (m. wt. 400 or 600) were charged in a 250–ml three-necked round bottom flask, fitted with condenser and mechanical stirrer. The reactants were stirred and slowly heated to a temperature of 170°C. The reaction mixture was maintained at this temperature for 5 h. Determination of the NaCl content, which increases gradually to reach a constant value at the end of the reaction, was used to follow the progress of the reaction. The product was then treated with an equal volume of saturated NaCl solution, neutralized with dilute HCl. The temperature of the mixture was then raised to 90°C and maintained for 1 h. The upper layer was separated and dried in vacuum oven at 50°C to a constant weight. The first set of polyoxyalkylated polyesters were C and D, which correspond to the products of the reaction of A with poly(ethylene glycol) 400 and 600, respectively. The second set of products were E and F, which correspond to the products of the reaction of B with poly (ethylene glycol) 400 and 600.

3. Dissolution of the Additives

The prepared copolymers were dissolved in free additive-base oil (SAE 30) to prepare the solutions for evaluation. In a conical flask, the desired weight of the polymer was added to 100 g base oil, then the mixture was allowed to stand overnight. This time was enough to procure the required swelling of the polymer. The conical flask was immersed in an oil bath placed on a thermostated hot plate fixed over a magnetic stirrer. The temperature of the oil bath was raised to 60°C and the mixture was vigorously stirred for 20 minutes.

4. Determination of Molecular Weight

The molecular weight of the prepared polyesters (A and B) was determined by Gel Permeation Chromatography (GPC), wasters 600 E.

5. Evaluation of the Prepared Polyoxyalkylated Polyesters as Lube Oil Additives

The evaluation was carried out by using the ASTM-D2270-87 method for measuring the viscosity index (VI). On the other hand, the ASTM-D 97-87 was used to measure the pour point on the Cold Filter Plugging and Pour Point Automatic Tester, model ISL CPP 97-2.

RESULTS AND DISCUSSIONS

1. Efficiency of the Prepared Compounds as Viscosity Index Improvers

The measured molecular weights of the prepared compounds are tabulated in Table 1. It is obvious from the data in this table that the molecular weight increases with increasing the molecular weight of the dibasic acid used for synthesis of the saturated polyester. The same finding is observed on the effect of the molecular weight of poly (ethylene glycol) reacted with the synthesized polyesters A and B.

The kinematic viscosity of the oil doped with different concentrations of the tested additives was determined at 40°C and 100°C. The

TABLE 1 The Molecular Weights of the Prepared Polyesters and their Polyoxyalkylated Products

Formula	Molecular weight	Ethylene oxid units, e.o,
A	1507	–
B	2690	–
C	2480	9
D	2879	13
E	3667	9
F	4063	13

concentrations ranged from 0.0 to 30 ppm. The VI increases with increased concentration of the polyester B additives in the solution as indicated in Figures 1 and 2. These figures reveal that polyester B exhibits the maximum efficiency at 30 ppm. This is because the solubility of the polymer generally increases with increasing temperature. In this instance the polymer molecules change from a tight coil to an expanded one as a result of increasing interaction between the polymer chain and the solvent molecules [33]. This increase in volume causes an increase in the viscosity of the mixture and offsets the normal reduction in viscosity of the oil with increasing temperature. Increasing the concentration of the polymer also leads to an increase in the total volume of polymer coils in the oil solution. Consequently, a high concentration of polymer will impart a higher viscosity index than a low concentration of the same polymer [34]. It can be seen from data that the additive F exhibits maximum VI improvement at 30 ppm and the corresponding VI value is 133. The reason for this excessive value may be attributed to the molecular weight of the additive F, which is larger than molecular weights of additives C, D and E. Figures 1 and 2 reveal too that the compounds prepared from polyester B afford VI value higher than that of the corresponding compounds based on polyester A. This also may be caused as a result of the effect of the molecular weight. This finding verifies the influence of the molecular weight on the effective coil radius of polymers and hence on the VI [35–38]. The effect of the number of ethylene oxide units on the VI is illustrated in Figure 3. It is obvious that, in all cases, the VI improvement increases regularly with the increase in the molecular weight of the synthesized additives.

2. Efficiency of the Prepared Compounds as Pour Point Depressants

All crude oils containing paraffin wax will eventually become non-fluid on chilling. This is caused by the precipitation of wax crystals as thin plates and needles, which overlap and interlock to form a three dimensional network. The pour point of an oil can be lowered by a dewaxing process. An addition of a pour point depressant in conjunction with the dewaxing is the most favored technique in lowering the pour point. These depressants obstruct the lateral crystal growth as a result of their adsorption on the precipitating wax [39, 40]. The prepared compounds were tested as pour point depressants (PPD). The experimental data are grouped in Tables 2 and 3 for a better understanding of the effect of different parameters, which will be discussed individually, on pour point (PP). The data Table 2 reveal that polyester

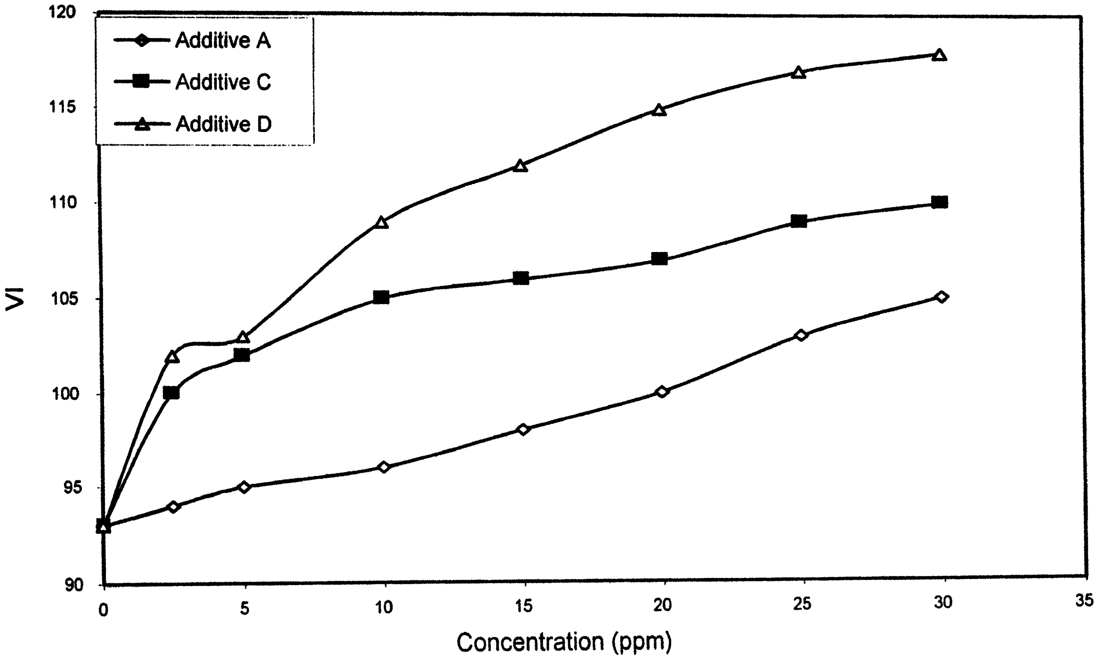

FIGURE 1 Effect of concentration VI for lube oil doped with 1,1′-Dipropyl succinate (A) and polyoxyalkylated 1,1′-Dipropyl succinates (C and D).

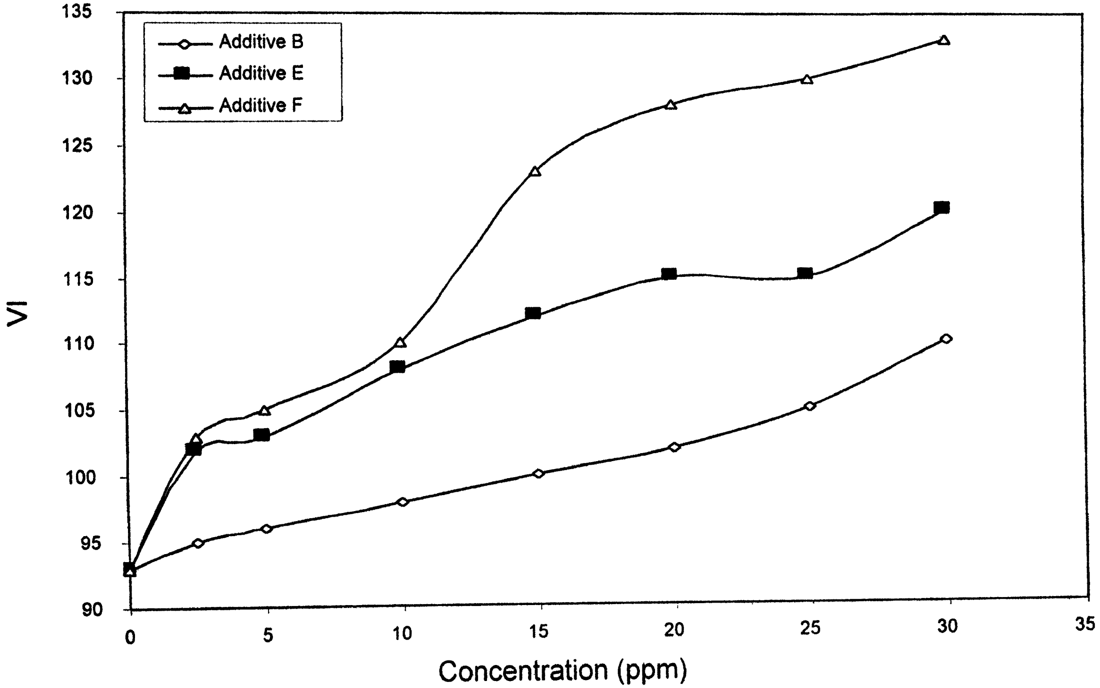

FIGURE 2 Effect of concentration on VI for lube oil doped with 1,1-Dipropyl sebaceate (B) and polyoxylakylated 1,1-Dipropysebaceates (E and F).

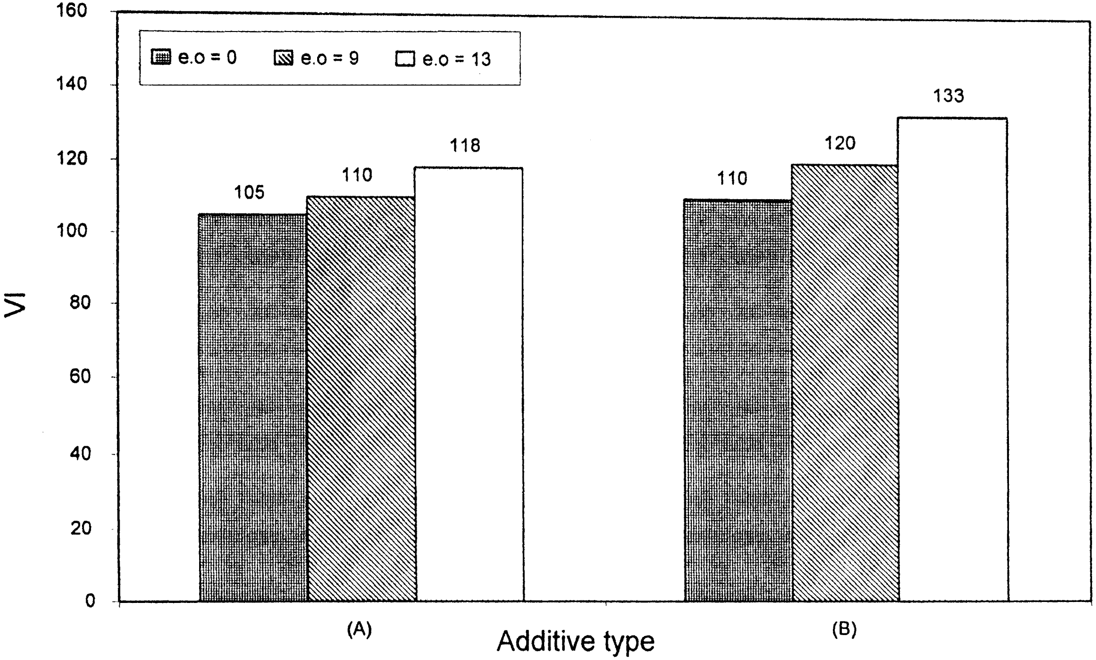

FIGURE 3 Effect of ethylene oxide units on the VI of A and B additives.

TABLE 2 Dependence of PP on the concentration of polyesters (A and B)

	Pour point (°C) in presence of:	
Conc. ppm	A	B
30.0	− 1	− 1
25.0	− 1	− 1
20.0	− 1	− 4
15.0	− 4	− 4
10.0	− 4	− 7
5.0	− 4	− 7
2.5	− 4	− 7
0.0	− 4	− 4

TABLE 3 Dependence of PP on the concentration of Polyoxylakylated polyesters (C, D, E and F)

	Pour point			
Conc. ppm	C	D	E	F
30.0	− 1	− 4	− 4	− 4
25.0	− 4	− 7	− 4	− 7
20.0	− 4	− 7	− 4	− 10
15.0	− 4	− 10	− 10	− 10
10.0	− 7	− 10	− 10	− 13
5.0	− 10	− 13	− 13	− 16
2.5	− 10	− 13	− 13	− 16
0.0	− 4	− 4	− 4	− 4

A has no effect on PP up to a concentration of 15 ppm. The increase in concentration to 30 ppm produced undesired PP results. This may be attributed to the difficulty of the dissolution of polyester A. On the other hand, polyester B exhibited minimum depression of PP (−7°C) at concentration from 2.5−10 ppm, then the PP increased at concentration 15 to 30 ppm. We speculate that this behavior may be a result of the adsorption of pour point depressants on the wax crystals surface. The resulting surface layer of pour point depressant hinders the growth of wax crystals and their capacity to adsorb the liquid oil to form gels. The limitations of pour point depressants are controlled by the nature of the lubricating oil and the concentration of the depressant itself.

Table 3, show the data of PP of the ethoxylated polyester polymers. This is easily explained by the solvating power of the oil. It is well understood that the solvating power of any solvent drops with lowering the temperature and vice versa. This reduction in the solvating power becomes more obvious when the molecular weight of the solute and its concentration increase. As a result of this lowering in solvating power, the polyester A and polyester B precipitate or form a gel and enhance the lateral crystal growth of the precipitated wax [40]. All polyesters and their ethoxylated derivatives show that concentration has the same influence on the PP, i.e., an increase in PP with increasing concentration. However, in general, with increasing concentration of any of the additives, the PP of the oil is reduced and reaches its lowest value at a particular concentration. When the concentration of the additive exceeds the optimum value, the PP of the oil starts to increase. This is explained, as mentioned before, by the solvating power of the oil. The data in Table 3 reveal that the increase of concentration from 0.0 to 2.5 ppm is accompanied by lowering the PP for the oil. The lowest concentration causes a lowering in the PP from − 4°C to − 16°C and is attained when additive F is used. This confirms the high potency of compound F as pour point depressant.

CONCLUSION

The following conclusions may be obtained from the data discussed heretofore:

- The VI increases with increased additive concentration.
- The effect of the polyoxyalkylated polyesters on VI increases with increased number of ethylene oxide units.
- Regardless of ethylene oxide units the polyester B afford higher values of VI than those obtained with polyester A additives.
- The VI for any polyoxyalkylated polyester E or F is higher than that for the corresponding polyoxyalkylated polyester C or D.
- All polyesters and their polyoxyalkylated polyesters show that the PP increases with increased concentration.
- The polyoxyalkylated polyesters based on polyester B are in general better PP depressants than the polyoxyalkylated polyesters based on polyester A.

REFERENCES

[1] Vamos, E. (1969). Theoretical Lubrication Eng. (Tribiology), I,II,III, Hung. Text Book Publishing Co., Budapest.

[2] Bowden, F. P. and Tabor, D. (1967). Friction and Lubrication, Methaen Co, Ltd., London.

[3] O'Conner, J. J. and Boyd, J. (1968). Standard Handbook of Lubrication Eng., McGraw–Hill, New York.

[4] Eckardt, H. et al. (1966). Additives, VEB, Deutscher Verlag fur Grundstoffindustris, Leipzing.

[5] Becker, P. (1965). Emulsions, Technical Publishing, Co., Budapest.

[6] V'amos, E. (1966). Temporary Corrosion Prevention With Fats and Cils, Technical Publishing Co.

[7] V'amos, E. (1978). Temporary Corrosion Prevention, Technical Publishing Co., Budapest.

[8] Dean, E. W., Baner, A. D. and Berglund, J. H. (1940). *Ind. Eng. Chem.* **32**, 102.

[9] Alkins, D. C. and Baker, H. R. (1947). *Ind. Eng. Chem.* **39**, 491.

[10] Glauis, F. J. (1950). *Ind. Eng. Chem.* **42**, 944.

[11] Dwans, F., Goldenberg, E. and Durand, I. R. (1976). US Patent, 3,959, 161.

[12] Lachowicz, D. R. and Holder, C. B. (1977). US Patent, 4, 026, 809.

[13] Schodel, U. (1986). "Viskositats - Index - Verbesserer - Typen and Wirkungsweise," 5th International Colloquium Technische Akademie, Esslingen.

[14] Neudoerfl, P. (1986). "Der Einstaz von Polymethacrylateten in Schmierolen aus Heutiger Sicht," 5th International Colloquium Technische Akademie, Esslingen.

[15] Neveu, C. and Huby, F. (1986). "Solution Properties of Polymethacrylate Viscosity Index Improvers.," 5th International Colloquium Technische Akademie, Esslingen.

[16] Nemes, N., Kovacs, M. and Kantor, I. (1986). "Vntersuchung der wirkung von File Bver Bessernden Additrven," 5th International Colloquium Technische Akademie, Esslingen.

[17] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1984). Second Proceeding of the Egyptian Conference of Chemical Engineering, Cairo, Egypt, March 18–20, p. 111–116.

[18] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1984). Proceeding of the Second Egyptian Conference of Chemical Engineering, Cairo, Egypt, March 18–20, p. 117–123.

[19] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1981). *Markromol. Chem., Rapid Commun.* **2**, 119.

[20] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1982). *Makromol. Chem., Rapid Commun.* **3**, 437.

[21] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1982). *Eur. Polym. J.* **18**, 735.

[22] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1982). *Polymer J.* **23**, 1859.

[23] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1983). *Polymer J.* **24**, 1308.

[24] Eckert, R. J. A and Covey, D. F. (1988). *Lubr. Sci.* **1**, 65.

[25] Graulin, G., Swire, E. A. and Jones, S. P. (1953). *Ind. Eng. Chem.* **48**, 2327.

[26] Graulin, G., Swire, E. A. and Jones, S. P. (1953). *Ind. Eng. Chem.* **48**, 2325.

[27] Lawrence, F. I. and Pohorilla, M. J. (1962). US Patent 3,036, 004.

[28] Sweeney, W. W. (1976). US Patent 3,947, 368.

[29] Corossland, R. K. and Clair, D. J. (1977). US Patent 4,032, 459.

[30] Byers, J. H. (1936). *Nat. Petrol. News* **28** (49), 83.

[31] Kaliehevsky, V. A. and Kobe, K. A. (1956). Petroleum Refining with Chemicals, Elseveir, New York.

[32] Vogel, A. (1975). Practical Organic Chemistry, Part 2, Logman, Harlow.

[33] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1983). *Polymer J.* **24**, 1429.

[34] Abdel-Azim, A. Abdel-Azim and Huglin, Malcolm B. (1984). *Polymer J.* **25**, 803.

[35] Abdel-Azim, A. Abdel-Azim (1993). *Polym. Bull.* **30**, 579.

[36] Abdel-Azim, A. Abdel-Azim (1994). *Macromol. Chem Phys.* **195**, 159.

[37] Abdel-Azim, A. Abdel-Azim (1994). *Macromol. Rapid Commun.* **15**, 183.

[38] Abdel-Azim, A. Abdel-Azim and Hassanein, Saiid A. (1995). 7th Conference on Aeronautical Sciences and Aviation Technology, Military Technical College, Kobry El-Kobba, Cairo, Egypt 2–5 May.

[39] Gavlin, G., Swire, E. A. and Jones, S. Jr. (1953). *Ind. Eng. Chem.* **45**, 2327.

[40] Lorensen, E. F. and Hewitt, W. A. (1962). *ACS Div. Pet. Chem.* **7**(4), 61.