SYNTHESIS AND APPLICATION OF POLYETHERS WITH MEDIUM-HIGH MOLECULAR WEIGHT

G. Chen[1], Q. Liu[1], J. Feng[1], G. Hu[1], P. Kois[2] and A. Perjessy[2]

[1]Department of Chemistry, Zhejiang University, Hangzhou, 310027, China
[2]Depertment of Organic Chemistry, Faculty of Natural Sciences,
Comenius University, 842 15 Bratislava, Slovak Republic

Abstract. *This paper describes a new type of catalytic system for synthesis of medium high molecular weight (MHMW) polyethers (MW 15000~20000). Low cost, short reaction time and easy to scale up are remarkable advantages of our procedure. The products were characterized by GPC, TG-DSC, X-Ray. The results showed that molecular weight distribution of the polyethers obtained by the new catalytic system are narrow. The polyethers with MHMW further reacted with long straight chain alkyl mono-glycidyl ether. The capped polyethers with terminal long chain alkoxyl are produced in the presence of alkaline catalyst. These polyethers are important components for preparation of water based hydraulic fluid. In addition the copolyethers with MHMW obtained by the reaction of polyethylene polyamine with ethylene oxide (EO) and/or propylene oxide (PO) were used as demulsifier for crude oil with very high thickness.*

Key words: *polyether, synthesis, water based hydraulic fluid*

Introduction

Unlike most polymers, polyethylene oxide is commercially available in an extraordinarily wide range of molecular weight from diethylene glycol up to polymers that have molecular weight more than several millions.

The classification of polyethers is shown as the following:

1. The wiscous liquid and waxy polymers with MW below about 6000, in which case the term lower MW polyethylene glycol (PEG) is used. These products are synthesized in the presence of KOH or NaOH.

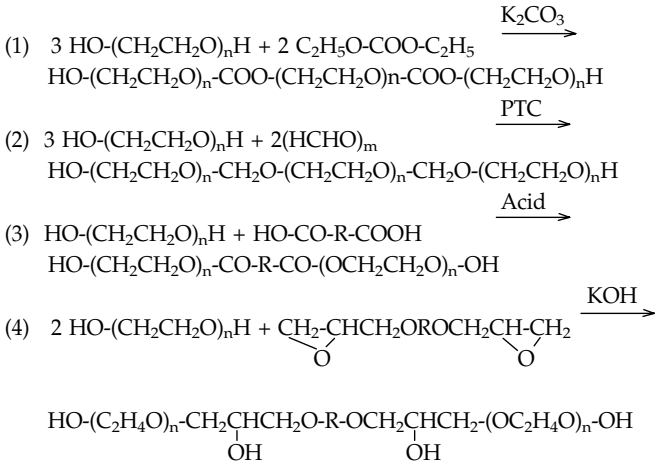
2. The hard waxy polymers with MW 6000~20000, in which case the term medium high molecular weight PEG are used. These products are usually produced by utilizing alkaline earth metal salts or hydroxides as catalysts.

3. The crystalline and thermoplastic polymers with ultrahigh molecular weight (several million or more) are called polyethylene oxide (PEO). The PEO are produced by utilizing a variety of special catalytical systems which consist of alkyl aluminium compounds, such as triethyl aluminium or triisobutyl aluminium with acetylacetone, secondary amine and water.

Well known fact is the polyethers with medium high molecular weight such as PEG 20000 are used as stationary phase for gas chromatography. At present, various novel application for the polyethers with MHMW are developing rapidly. It was found that the polyethers with MHMW are very important intermediates for water based thickness in cosmetic industry, water based hydraulic fluid which can be used instead of petroleum fraction for lubricant usage, a special polymer demulsifiers for crude oil with higher thickness, antistatic agents for synthetic fabric in textile industry, and a prepolymers for polymerization of polyurethane.

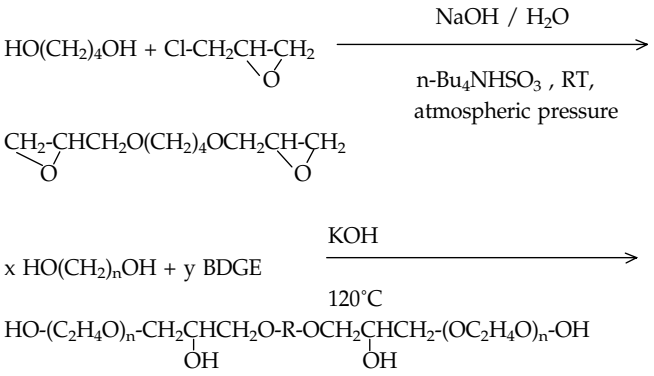
General survey of synthesis of MH-polyethers

Crosslinking method. The main problem of this method is the gel product sometimes obtained by intermolecular crosslinking reactions of hydroxyl groups. The reaction is not easy to control, especially in a pilot scale. We decided to improve the crosslinking method and to select catalytical systems for one step synthesis of MHMV polyethers.



R-: -$(CH_2)_4$-, alkylene, O-C_6H_4-$C(CH_3)_2$-C_6H_4O (Bisphenol A unit)

Synthesis of 1,4-butylene diglycidyl ether (BDGE)



One step polymerization. A number of catalytic systems are known for synthesis of medium high molecular weight polyethers. The relative data for comparison of various methods are shown in Table 1. For bulk and solution polymerization we use 0.5 and 2 liter steel autoclaves equiped with magnetic stirrer, heating jacket and internal cooling coil. EO and PO are from Jin Ling, China Petroleum Chem. Co.

Bulk polymerization. The MH-01 catalytic system was prepared in our laboratory. MH-01 was first dried in oven heating to 150°C for 12 hours, and then charged to an autoclave. The autoclave is evacuated and purged with inert gas N2. Then ethylene oxide (EO) is gradually added to the autoclave and set up to the working pressure. The EO are polymerized by heating at 110 ± 10°C for 6 hours. After the ring-open polymerization of EO is completed, the polyether product is further treated by neutralization using alkaline and/or decolorisation using active charcoal, respectively. In case of bulk polymerization the viscosity of PEG 15000–20000 at 100°C ranges from 0.5 to 1x 10^5 CP. It is difficult to circulate high viscous PEG products through an autoclave.

The another problem is necessary to remove excess of polymerization heat to avoid all possibilities of explosion.

Solution polymerization. The catalytic system MH-02 was prepared in our lab. MH-02 consists of alkaline earth metal salt and cocatalyst for solution polymerization of EO and/or PO. Except the solvent, such as toluene or xylene, the procedure is the same as for bulk polymerization.

Results and Discussion

The choice of catalytic system and reaction condition. The key to the synthesis of PEG of certain molecular weight lies in the choice of suitable catalytic system. According to many examples in literature, it is possible to synthesize the medium high molecular weight PEG with the alkaline catalysts as KOH, $Ba(OH)_2$, or Lewis acids like $FeCl_3$, $AlCl_3$, $ZnCl_2$ and $SbCl_5$. However, it was found that influence of water and air on EO is not easy to control and the molecular weight of the products are always lower than we expected.

It was also reported that PEG with the molecular weight of 20000 was produced in the presence of alkaline earth carbonates such as $CaCO_3$, $SrCO_3$, $BaCO_3$ or sulphates, such as $CaSO_4$, but the activity of such catalyst was lower. The reactions needed long reaction period and obtained yield of products were poor. What is more, the initiation of polymerization was readily inhibited in the presence of adsorbed anions such as chlorate, nitrate and thiosulfate.

There are a number of catalysts for the synthesis of high molecular weight PEO, in addition to those mentioned above, among them often used are alkyl aluminium, aluminium alkoxides, alkyl aluminium combined with gypsum. We used these catalyst for preparation of MHMW polyethers 20000, but the molecular weight is much higher than 20,000.

The effect of concentration and composition of the MH-01 catalytic system on the molecular weight of PEG and initiated period. Figure 1 shows that MW decreases with the increase of concentration of MH-01 catalytic system under the given ratio of cat./cocat. (5/1).

From Figure 2, we found that the initiated period could be shorter than that of 10/1 when the ratio of cat./cocat. equals to 5/1. In the presence of catalyst or cocatalyst only, we also observed from Figure 2 and Figure 3 that longer initiated period and lower molecular weight of PEG.

The effect of water in EO and MH-01 catalytic system on the polymerization and molecular weight of PEG. Figure 4 indicates that the optimum catalytic activity for the preparation of medium-high molecular weight PEG is only when the content of water in MH-01 being 0.02~0.05 H_2O(g)/cat.(g), which is just sufficient to form physical adsorption on the catalyst.

Table 1. The comparison of various catalytic systems for synthesis of MHMW polyethers

No	Catalytic system	Temp (°C)	Pressure (MPa)	Time (hr)	Molecular weight	Yield (%)
1	**MH-01****	110–120	0.6~1.0	6 7	1.5~2 x 10^4	>90
2	KOH	120	0.6	26	5200	>90
3	$ZnCl_2$, $SbCl_5$	120	1.3	6~8	5600	>85
4	$SrCO_3$	110	3.0	20	10^5–10^6	70
5	$BaCO_3$	100	3.0	24	>10^5	67
6	CaSO4	200	3.0	24	10^5	73
7	$AlEt_3$–$CaSO_4$	120	<1.0	>15	4 x 10^4	76
8	Al(i-Bu)3-H2O-AcAc	70	0.6	6~8	>10^6	>90

*Literature value; **average value of 5 experiments in our laboratory

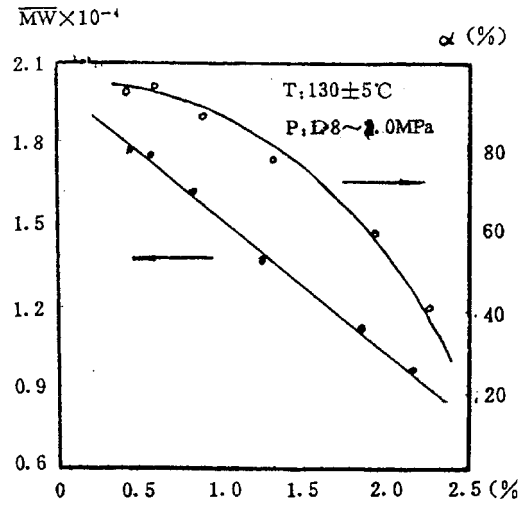


Figure 1. Effect of concentration of MH-01 on the MW of PEG

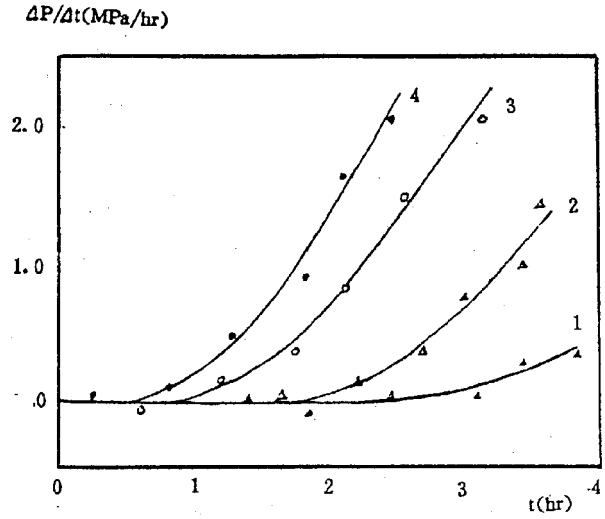


Figure 2. Effect of composition of MH-01 on initiated period
1 – catalyst only; 2-cocatalyst only;
3 – catalyst/cocatalyst:10/1;
4 – catalyst/cocatalyst:5/1.

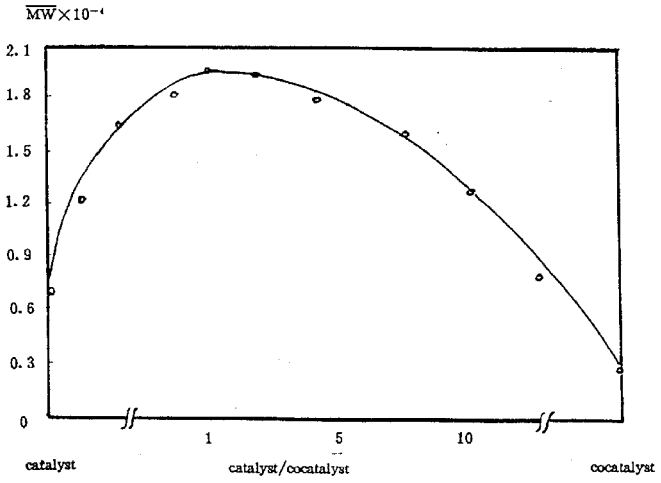


Figure 3. Effect of the composition of MH-01 on the MW of PEG

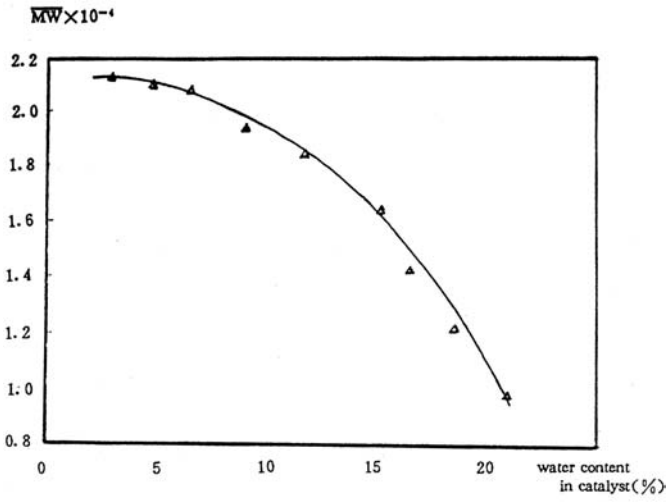


Figure 4. Effect of the water content of MH-01 catalytic system on the MW of PEG

Figure 5. GPC peak shapes of PEG, (a) PEG (control); (b) PEG (syn.)

Molecular weight and its distribution of PEG in table 2 is the retention time of various standard samples by GPC. From the data in Table 2 we get the linear correlation coefficient, 0.9964. By comparison of control sample PEG (made by Shanghai Chemicals company) and PEG synthesized in our lab, we found the both GPC peak shapes are similar.

The molecular weight of synthesized PEG is close to the control PEG. The d value (distribution coefficient) is smaller than the value of control PEG.

The crystallinity (Xc) of PEG. Crystallinity is the proportion of the crystallinic part of the whole polymer. From the Figure 6a, b is clear the synthesized sample is very similar to control PEG.

Thermal analysis of PEG. Figure 7 presents the thermal analysis diagram of PEG. The curve shows the value of both melting point (m.p.) and enthalpy (ΔH) are almost the same for both samples.

The ^{1}H-NMR spectrum is done by FX-90MHz NMR.

Table 2. Standard samples and the corresponding retention time

Standard samples	PEG 6000	PEG 10000	PEG 20000
Retention time (min)	22.2	21.85	21.00

*Gas Chromatography Grade

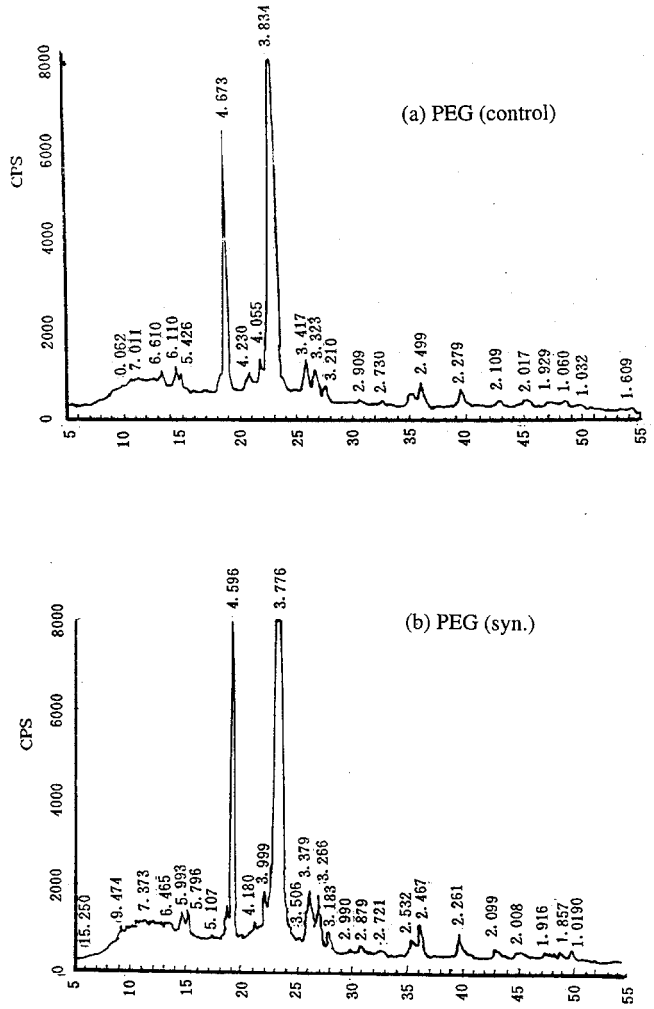


Figure 6. X -ray diffraction diagram of PEG, (a) PEG (control), (b) PEG (synth.)

The clearly detectable signal at 1.1~1.2 ppm is due to three protons of methyl at polyoxypropylene unit, and at 3.4~3.6 ppm corresponds to seven protons of methylene and methylidyne at polyoxyethylene and polyoxypropylene unit. The ratios of EO/PO are calculated as follows:

$$EO / PO\ (w / w) = 33(S_B\text{-}S_A) / 58S_A$$

IR spectrum of the random copolyether is done by 5DX-FTIR (shown in Figure 9). The structural assignments can be correlated with the band frequencies represented in the following equation:

$$EO / PO\ (w/w) = 4.63\text{-}1.98A_{1373} / A_{1350}$$

Epoxides with $-CH_3$ and $-OCH_2$ bonds show band absorption because of $-CH_3$ symmetric bending vibration at 1730cm^{-1} and $-OCH_2$ plane rocking vibration at 1350cm^{-1}, respectively.

Application

Our efforts were limited to the water based and enviromentally friendly compounds with good market perspectives and also aimed to develop a new hydraulic

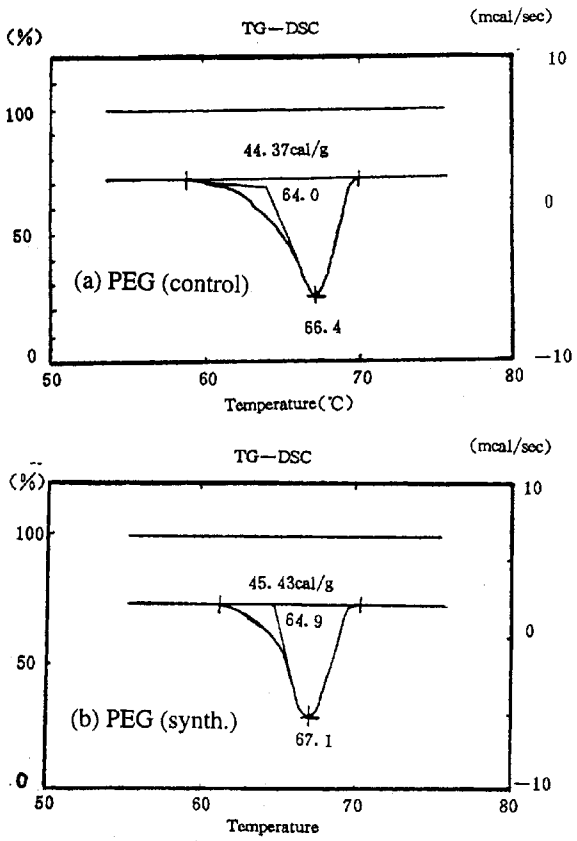


Figure 7. Thermal analysis of PEG

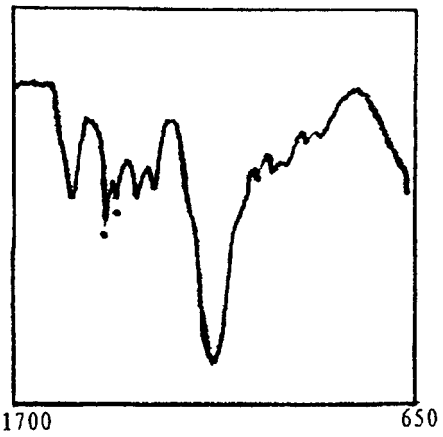


Figure 8. 1H-NMR diagram of PEG

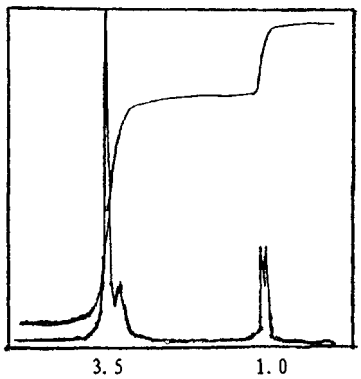


Figure 9. IR Spectrum of PEG

Table 3. Results of EO/PO (w/w) determined by IR and ^{1}H-NMR

EO/PO (w / w)	A_{1373}/A_{1350} (IR)	EO/PO (w/w) (^{1}H-NMR)	EO/PO (w/w) (calculated value)
6 : 4	1.56	1.55	1.54
5 : 5	1.70	1.24	1.26
4 : 6	1.90	0.88	0.87
3 : 7	1.95	0.77	0.77

fluid. The formula of water based hydraulic fluid usually contains the following ingredents:

(1) Polyether with capping group as thickener.
(2) Extreme pressure/ antiwear additives
(3) Corrosion inhibitors
(4) Metal deactivators
(5) Demulsifers
(6) Antifoam agents
(7) Antioxidants

The capping polyether thickeners (CPT) are synthesized by reaction of MHPE (MW.20000) with long chain alkyl glycidyl ethers (AGE).

$$\text{nEO} \xrightarrow{\text{MH-02}} \text{PEG 20000}$$

$$\text{ROH + ECH} \xrightarrow{\text{KOH}} \text{AGE}$$

$$\text{AGE + PEG 20000} \xrightarrow{\text{KOH}} \text{CPT}$$

The flow properties for CPT solution were determined. It was found that the viscosity of CPT solution increased with increasing molecular weight of polyether, carbon atom number of alkyl, carbon chain number of alkyl, and concentration of CPT. The solution properties of CPT in water are different from ethylene glycol solution.

(1) Effect of carbon number of alkyl in AGE on the viscosity of CPT in water-ethylene glycol solution is shown in Fig.10. In Fig.10, n is carbon number of alkyl in AGE . Among them, when n=0 the viscosity of CPT equals to the viscosity of PEG 20000 without capping groups. The viscosity of CPT from C12 alkyl to C16 alkyl gradually increased with carbon chain length in the alkyl. The highest viscosity of CPT was observed from C16 alkyl to C18 alkyl. The reason might be that PEG was terminated by long chain hydrophobic alkyl group to form macro-molecular micella which are favorable to intereaction and increasing the solution viscosity of CPT.

(2) Effect of molecular weight of MHPE on the viscosity of MHPE in water solution is shown in Fig. 11. From this figure it was found that PEG 20000 has much higher viscosity than PEG 6000.

(3) Effect of weight ratios of water and ethylene glycol on the viscosity of CPT solution. The results are shown as Figure 12. It was found that viscosity of CPT solution decreased with increasing of concentration of ethylene glycol. The viscosity of CPT solution also decreased with increasing the shear rate (lgD).

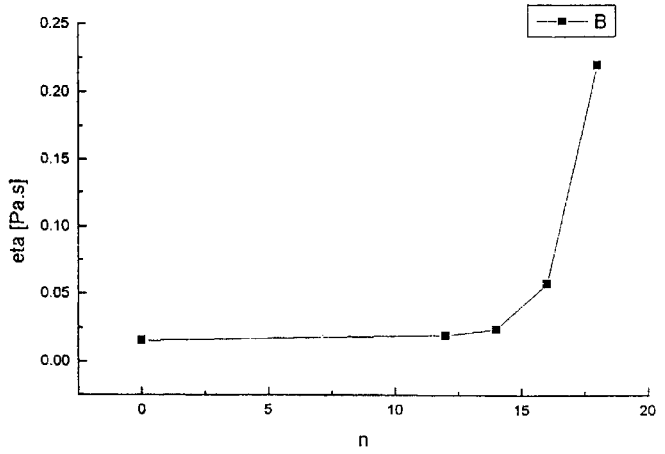


Figure 10. Effect of carbon number of alkyl in AGE on the viscosity of CPT in water-EG solution at 40°C; H_2O / EG = 1.16

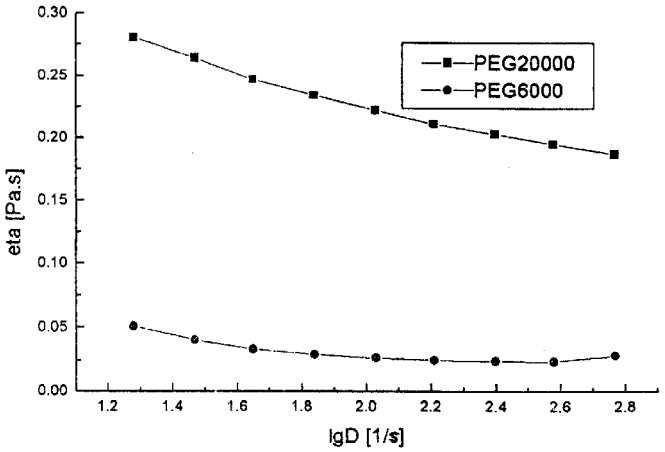


Figure 11. Effect of molecular weight of PEG on the viscosity of CPT in water-EG solution; Cp = 3% ; H_2O / EG = 1.16 ; T = 40°C

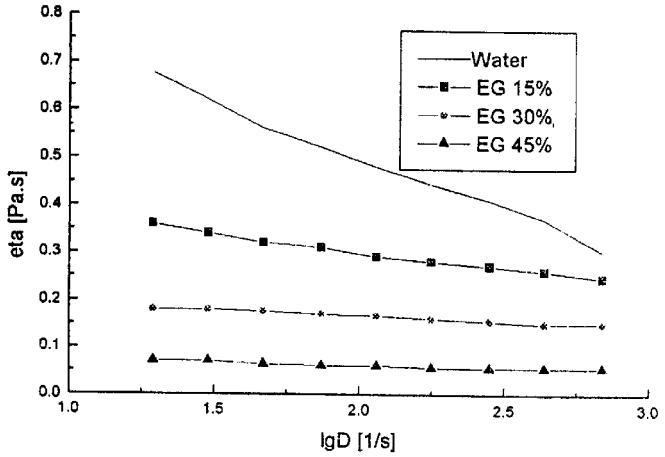


Figure 12. Effect of weight ratios of water and EG on the wiscosity of CPT solution, Cp = 3%, T = 40°C

Conclusions

(1) PEG 20000 are synthesised by the solution polymerization in the presence of MH-01 catalytic system at 120(10˚C for 6~8 hours; the MW distribution is narrow.

(2) The copolymers of EO/PO with different ratios are synthesized by bulk and/or solution polymerization in the presence of MH-02 system at 120(10˚C for 6~8 hours.

(3) The PEG 20000 and copolymer of EO/PO are characterized by IR, 1H-NMR, GPC, TG-DSC, and X-ray. The PEGs in the MW range of 15000-20000 can be obtained by the new catalytic system. The molecular weight distribution is narrow which is suitable for water based hydraulic fluids.

(3) Synthesis and application of water based hydraulic fluid is briefly described, and the solution properties are also determined.

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