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Synthesis and Characterization of Olefin Copolymers as Viscosity Modifiers for Engine Oil

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ABSTRACT

Microstructural properties of olefin copolymers (i.e., copolymer composition, sequence distribution, and molecular weight and its dispersity) are key factors, which affect the behaviour of olefin copolymers as viscosity modifiers in engine oil. In this article, the variation procedure and control methods of these specifications are described for the synthesis of olefin copolymers using soluble Ziegler-Natta catalyst in a semibatch reactor. Solution copolymerization of ethylene/propylene was performed using $VOCl_3$-$Al_2Et_3Cl_3$ systems. Finally, the synthesized viscosity modifier was characterized by IR, GPC, ^{13}C NMR, DSC, and XRD techniques and elemental analysis method. Molecular weight was controlled by continuous feed of hydrogen during the reaction and its narrow dispersity was maintained by catalyst specifications and initial saturation of solvent by monomers. Although catalyst activity varies with time, ^{13}C NMR and IR results demonstrated steady copolymer composition. This was achieved by using a catalyst system with mostly single active site in a semi-batch polymerization by feeding monomers continuously. Also, it was found that randomness in the microstructure of the copolymer was induced at a specific monomer ratio.

Key Words:
olefin copolymer;
Ziegler-Natta catalyst;
viscosity modifier;
semi-batch polymerization;
microstructural properties.

INTRODUCTION

Oil undergoes temporary viscosity changes under operating conditions in engines. Therefore, multigrade automotive lubricants usually contain polymeric additives called viscosity modifiers (VM; previously known as viscosity index improvers or VII). These are oil soluble polymers, which enable the oil to provide adequate hydrodynamic lubrication at high temperatures and good starting/pumping performance at low temperatures. The mechanism of VII operation has been postulated by

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various researchers, i.e., Selby and Muller [1-6]. VM improves the viscosity index (VI). This function depends not only on particular polymer chemistry and constitution but also on shear rate and temperature [7]. ASTM D 2270-Procedure B describes the procedure for calculating the thickening efficiency and viscosity index of petroleum products.

As the polymer chains break under the load, VII tolerates a permanent viscosity loss beneath the mechanical shear stresses at service conditions. The most common measure of lubricant degradation in service is kinematics viscosity. The reduction in kinematics viscosity, reported as percent loss of the initial kinematics viscosity, is a measure of shear stability of the polymer containing fluid as given in ASTM D 3945 [1].

Olefin copolymers (OCP) constitute one of the most important class of polymers used as VII. They are oil soluble copolymers comprising ethylene and propylene and may contain a third monomer, a nonconjugated diene. Although, ethylene/propylene copolymers represent the simplest case of vinyl copolymers, the structure of these copolymers can be extremely complex. Despite related chemical structures, these copolymers exhibit different properties and they have commercial significance [2-7].

The chemical and associated physical characteristics, which make these copolymers suitable for using as VIIs, include molecular weight and its distribution, ethylene-to-propylene ratio, and comonomer sequence distribution. Therefore, the chemical nature of a given polymer needs to be understood for designing an effective multigrade formulation. Not only the appropriate range of weight average molecular weight (50,000-200,000 g/mol) but also the low polydispersity index (PDI) are the most important factors in control of the shear stability of OCPs. High molecular weight copolymers with broad PDI are able to increase permanent viscosity loss by concentrating the mechanical stress for molecular chain scission [6]. Further, the amount of branching can also be critical to the polymer behaviour. Nonconjugated dienes are often used in the manufacture of ethylene-propylene copolymers to provide a site for cross-linking (in non-lubricant applications) or to reduce the tackiness of the rubber for ease of manufacturing and handling.

Certain dienes promote long-chain branching. A disadvantage of long-chain branching is that it reduces the lubricating oil thickening efficiency and shear stability relative to simple copolymer of similar molecular weight and copolymer composition [6]. With a fixed arm length, an OCP having the higher degree of branching, increases the viscosity index rather than the one having a lower degree of branching. On the other hand, the viscosity index increases with increase in the arm length when the degree of branching is fixed. Adding OCP also causes a change in the pour point of the lubricant oil. The pour point decreases with increase in the degree of branching [8].

The specific grade of olefin copolymer is used as VII, which has low (40-60 mol%) propylene content [5]. This is a desirable characteristic for VII, because the propylene unit (with α-hydrogen) is the point of attack by any oxidative degradation that occurs during its service in the engine. Consequently, oil undergoes more rapid and higher degree of permanent viscosity loss in engines. Hence, the thermo-oxidative degradation of the macromolecules is also related to the structural features.

Due to the higher reactivity of ethylene to propylene, the formation of long sequences of ethylene is favoured rather than propylene sequences. This is substantiated by ^{13}C NMR spectroscopy technique [6]. Also, higher content of ethylene or propylene blocks in polymer chain, which in turn increases crystallinity in the VII, leads to problems at low temperature. For optimum performance, amorphous polymers must contain less than 10% crystallinity. The longer sequence distribution of any monomer affects both the low and high temperature properties of the VII [7]. In addition, the arrangement of monomers must be random along the copolymer chain [5].

The most common methods for manufacturing OCP viscosity modifiers are solution process and gas-phase process which are not appropriate for this purpose [6]. Homogeneous Ziegler-Natta catalysts are soluble in the reaction medium. Therefore, they function more efficiently because all molecules serve as potential reaction sites. Usually soluble Ziegler-Natta or metallocene catalysts are used for synthesizing random olefin copolymers in solution process [8-10]. $VOCl_3$-$Al_2Et_3Cl_3$ forms a soluble Ziegler-Natta catalyst system with mostly a single active site. The number of active centres is around 15-40% of the initial $VOCl_3$ concentration, which allows easy incorporation of

propylene by low PDI into random and narrow comonomer distribution [10-12].

There are many reviews available in the literature either on ethylene-propylene copolymerization by Ziegler-Natta catalysts [10-21] or characterization of OCPs as VII [22-25]. Because of immense commercial significance, it is necessary to obtain desirable properties of OCP as VII during synthesis. In this work we synthesized vanadium catalyzed olefin copolymers using a semibatch bubble column reactor and determined the specifications of the resulting polymer chains as a VM.

EXPERIMENTAL

Chemicals

Ethylene, propylene and hydrogen were purchased from Electrochem Co. (polymerization grade) with purity>99.9%. Heptane (>99%), soluble $VOC1_3$ (>99.5%) and co-catalyst $Al_2Et_3Cl_3$ (97%) were bought from Merck.

Polymerization System

Polymerization unit is shown in Figure 1. The solution polymerization was carried out in a 300 mL stainless steel bubble column reactor using n-heptane as the solvent.

At first, the solvent was saturated with monomers and hydrogen (gas phase) with specified ratios. Then, the required amount of the vanadium compound ($VOCl_3$) and cocatalyst ($Al_2Et_3Cl_3$) were introduced into a glass reservoir containing n-heptane (10-15 mL) at 25°C under positive pressure of nitrogen. The activity of this catalytic system maximize some minutes after the introduction of catalyst portions. It is related to molar ratio of cocatalyst/catalyst (Al/V) and quantity of comonomer.

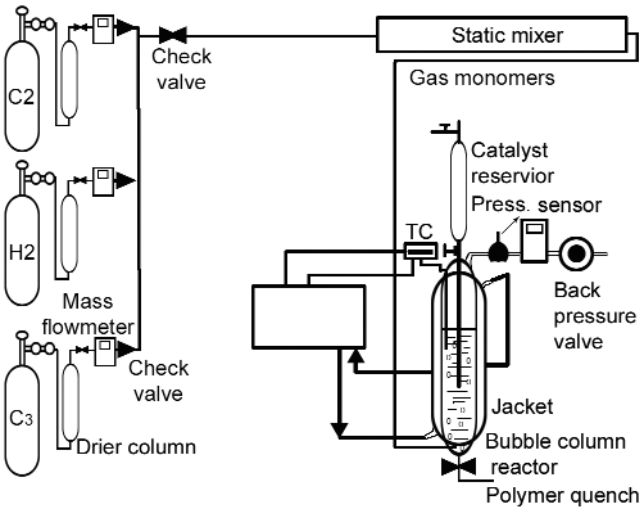

Figure 1. Schematic view of polymerization system.

Based on the systematic procedure, we have derived and adjusted the optimum values of reaction conditions for ethylene-propylene copolymerization by this catalytic system through many tests. Then, the conditions were adjusted by these optimum values. Under constant gauge pressure (1 ± 0.1 atm) and temperature (22 ± 1°C), the reaction was initiated with the injection of the aged catalyst at its highest activity to attain the low molecular weight with narrow dispersity and random microstructure for copolymer as viscosity modifier grade. The gas phase was fed continuously under a constant rate, while the liquid phase (solvent, catalyst and co-catalyst) was operated in batch to guarantee a constant feed composition in reaction medium and to produce a homogeneous copolymer. A constant pressure was maintained during the reaction and a manually controlled back pressure regulator vented off excess monomers. The composition homogeneity was maintained due to the initial saturation of solvent and higher mass transfer rates of monomers than copolymerization rate.

After a specific time, the resulting reaction medium contained ~2 wt% of soluble copolymer which prevented undesired rheological effects on the kinetic of the reaction. At the end of the reaction, the feed streams were shut off and isopropanol was added to quench the reaction for precipitating the soluble polymer. Then the precipitated polymer was separated, washed with excess isopropanol and vacuum-dried at 40-70°C for 24 h.

The one factor at a time method was applied to study the effect of process variables on the key properties of synthesized polymer (i.e., copolymer composition, sequence distribution, and molecular weight and its dispersity). Finally, the optimum conditions were applied to produce OCP as VM and the properties of the resulting polymer were measured. The optimum conditions are listed in Table 1.

Copolymer Characterization

Polymer films (0.18-0.2 mm) were characterized for

Table 1. The values of optimum conditions.

Variables	Values	Initial conditions	Values
[Catalyst] (mol/L)	7.210E-5	Hs (mol/L)	0.048
Al_0/VO_0	28.680	Es (mol/L)	0.021
[P]/[E]	19.048	Ps (mol/L)	0.411
T_{SET} (°C)	22	PSET(abs) (bar)	2

ethylene incorporation by infrared spectroscopy (IR) using a Perkin Elmer 2100 spectrometer. This was achieved by measuring the ratio of the intensities of the 1155cm^{-1} methyl band and 720cm^{-1} methylene band according to ASTM D 3900.

^{13}C NMR spectormeter Brucker ACP 500 MHz with $CDC1_3$ at 50ºC was used to identify more accurately the ethylene content and sequence distribution of the synthesized copolymer [7, 22-23].

Molecular weight and its distribution were determined by gel permeation chromatography (Waters 150C ALC/GPC) in THF at 30□C. The data were analyzed using polystyrene calibration curves.

Thickening efficiency (ASTM D 445), VI (ASTM D 2270B), and shear stability (ASTM D 3945) were measured for a 1.5 wt% polymer solutions in oil.

Differential scanning calorimetry (12000 PL-DSC) at a heating rate of 10□C/min was used to determine the specific heat capacity (Cp) of the copolymer, enthalpy, and entropy of copolymerization reaction [24-25].

XRD was used to obtain crystalline content of the mainly amorphous copolymers.

RESULTS AND DISCUSSION

Microstructure Characteristics

Molecular Weight and its Dispersity

Molecular weight plays the main role in thickening efficiency and shear stability of OCPs used as VII. As shown in Figure 2, the initial period in olefin copolymerization is often characterized by a gradual increase in the polymer molecular weight up to some constant value. This behaviour is typical of olefin polymerization carried out at moderate temperatures (<50ºC) and low monomer concentration in the presence of active catalytic systems [20].

The initial increase of molecular weight is approximately regarded as □quasi-living□ chain growth. When

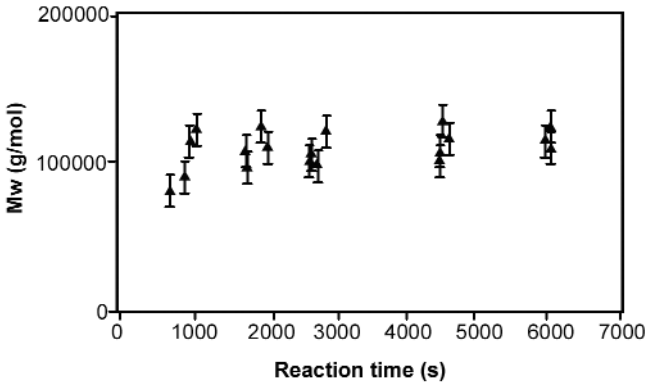

Figure 2. The variation of copolymer molecular weight vs. reaction time at the experimental conditions given in Table 1.

reaction rates of chain initiation and termination reach equilibrium, molecular weight becomes time independent under stationary conditions. If the process is carried out at relatively low temperatures, the molecular weight growth can be observed even for a few hours. At high monomer concentrations, the stage of molecular weight time independence appears at shorter period of time, which causes narrower molecular polydispersity. A detailed description of these phenomena is given by Kissin [20].

Molecular weight control in a suitable range (50,000-200,000 g/mol) is achieved by intensifying the chain transfer reaction (i.e., by hydrogen, Al/V ratio,and co-solvents). In olefin copolymerization, ethylene shows the highest reactivity in the propagation step and hence it will display propagation behaviour rather than transferring or termination. Thus, the ethylene exhibits negligible tendency to chain transfer reactions, compared to propylene [10-11,21].Therefore, chain transfer reactions to monomer occurs only due to propylene with little efficiency to control molecular weight [21].

Hydrogen is known to be the best chain transfer agent in Ziegler-Natta polymerization but very often its effect transcends that of a mere chain transfer agent, since it might affect the polymerization rate and polymer microstructure significantly [14-15].

Although, all chain transfer agents (hydrogen, propylene and alkylaluminium) were present in the system, but hydrogen indicates higher transfer ability and mainly controls the chain growth. The use of hydrogen as a molecular weight controlling agent is described in Figure 3. It can be seen that the molecular weight

approaches a plateau limit for the effect of hydrogen as chain transfer agent. This behaviour can be attributed either to the lower magnitude of the rate constant of the chain transfer via hydrogen than the average rate constants of propagation or to the limitation of hydrogen concentration in heptane at the adjusted reaction conditions [11, 21, 26].

Also, alkyl chain transfer effects were taken into account in copolymerization kinetic when Al/VO ratio was varied from 2 to 64. It was noticed that, for Al/VO ratios lower than 2, no significant yield can be obtained. At least 2 alkylaluminium molecules and 1 vanadium salt molecule are required to form the active species as reported in literature [21]. As indicated by experimental results, the alkyl chain transfer's effect on molecular weight was intensified by the excess of alkyl when Al/VO ratio (~28) was used at higher value than the optimum value (~8). Figure 4 demonstrates the verified influence of Al/VO ratio on the molecular weight.

In order to increase the shear stability and life time of synthesized copolymer in lubricating service, it is necessary to produce monodisperse copolymers. The nature of this catalyst complex and mostly its single active site for polymerization allows easy incorporation of alpha olefins into random ethylene copolymers, characterized by narrow molecular weight distributions and narrow co-monomer distributions. Highly active catalyst system, intensive mixing or higher concentration of monomers have been used to improve either monomer conversions, yield and rate of copolymerization or PDI of OCP [11, 18, 21, 26]. Since chain transfer by hydrogen and excess of alkyl do not affect the OCPs molecular weight considerably to control such conditions, we postulated that chain transfer to co-solvent might manage the molecular weight in solution polymerization. It was found that the addition of a low amount of toluene (<5 wt%) could be useful for reducing the molecular weight. Therefore, it can be concluded that toluene acts as chain transfer for this copolymerization system.

It is accepted that the molecular weight is determined by the ratio of the rate of propagation reaction to the rates of chain transfer and termination reactions. Also, monomer concentrations have important effects on these steps. It is obvious that monomer concentrations affect this ratio. Consequently, the molecular weight and its dispersity change undesirably when unsteady variations occur in the proportion of ethylene/propylene concentrations. The application of a continuous system for monomers with high mass transfer rate and a batch system for catalyst would prevent composition drift of monomers in reaction and also homogenize the distribution of catalyst activity variations. The best conditions are initial saturation of solvent by monomers and injection of the catalyst at its highest activity in one shot, which stabilize the molecular weight and give narrow dispersity. These strategies reduced PDI to 1.8 as is shown in Figure 5.

Copolymer Composition

Cozewith et al. modeled the ethylene-propylene copolymerization by using a plug flow reactor (PFR) and observed that the compositional distribution was not homogeneous due to ethylene-propylene ratio vari-

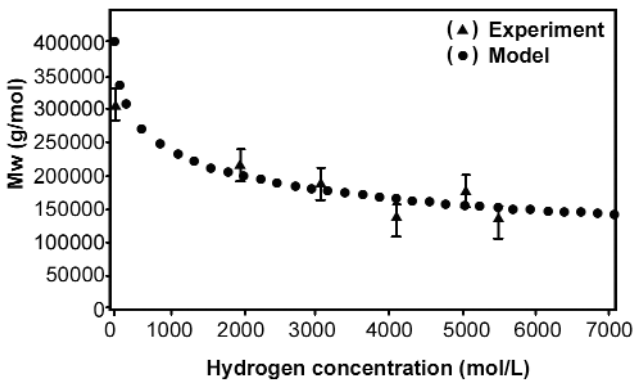

Figure 3. Hydrogen's effect on copolymer molecular weight (Al/V=8.314, V=7.2E-5 (mol/L), t=5400 (s), [E]= 0.04838 (mol/L), [P]/[E]=10.988, temperature = 22°C.

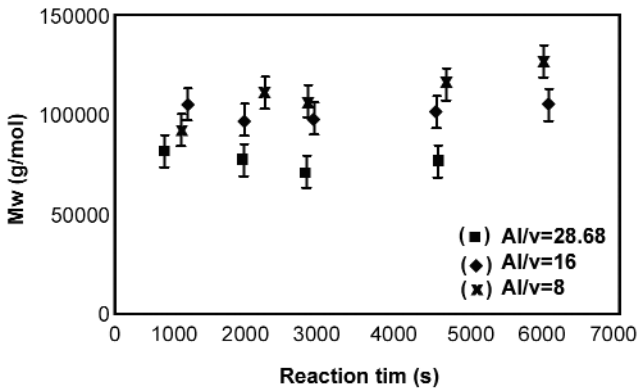

Figure 4. Alkyl aluminium's effect on copolymer molecular weight with reaction time at the experimental conditions given in Table 1.

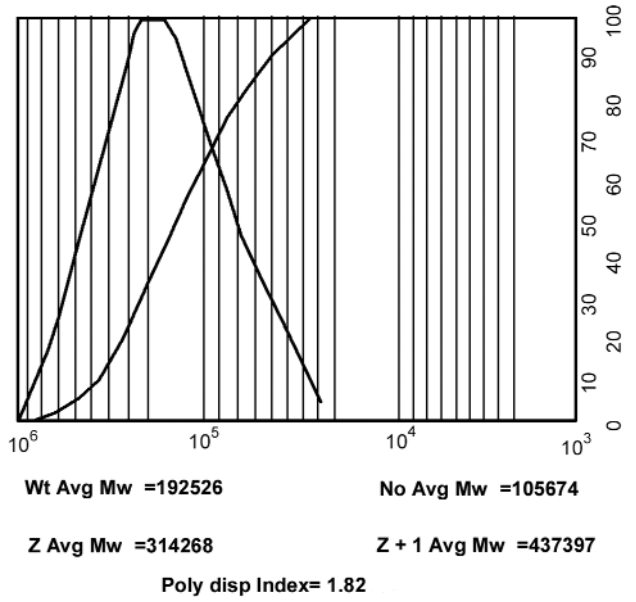

Figure 5. GPC Diagram of synthesized olefin copolymer at the experimental conditions given in Table 1.

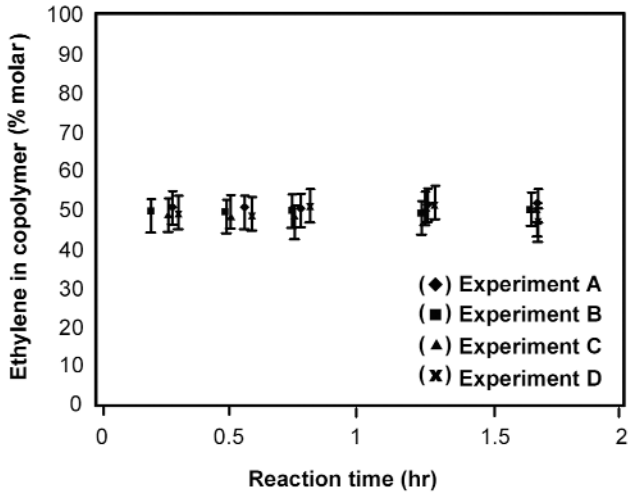

Figure 6. The variation of copolymer ethylene content vs. reaction time at the experimental conditions given in Table 1.

ation (composition drift) in the reactor, as ethylene is more reactive than propylene [11]. Already, it was explained that the high ethylene content (i.e., its blocks) in copolymer composition increases the crystallinity of polymer which in turn leads to problems when OCPs are used as VM at low temperatures. The copolymers must contain 30-40 wt% (45-60 mol%) of ethylene in random distribution and less than 10% crystallinity [5,7].

As is shown in Figure 6, ^{13}C NMR and IR data imply that the ethylene content of copolymer is constant during polymerization. This composition homogeneity is an outcome of constant concentration of the monomers (due to the initial saturation of solvent with monomers) and high mass transfer rates of monomers, which satisfy steady concentration during reaction [11].

Number Average Sequence Lengths

Microstructural parameters, (such as number average sequence length and sequence number) were obtained by using the triad sequence distributions [7, 22-23] revealed by ^{13}C NMR spectroscopy for 18 different samples of synthesized OCP at various reaction time intervals. A typical ^{13}C NMR spectrum is shown in Figure7 and its result is included in Table 2. A very important feature emerging from the sequence distribution of these samples is the absence of any longer sequences of E or P-units, i.e., the concentration of

Table 2. Assignment of various resonance signals and integral intensity of synthesized OCPs at different reaction time period using the triad sequence distributions from ^{13}CNMR spectroscopy.

Region	Range (ppm)	Assignment	Integral intensity
A	45-48	$\alpha\alpha$-CH_2(PPP, PPPE, EPPE)	0.31-0.51
B	36-39	$\alpha\gamma,\alpha\delta$-$CH_2$(EPEP+PEPE, PPEP+PEPP, EPEE+EPPE, PPEE+EEPP)	2.82-3.94
C	33.5	-CH(EPE)	1.85-2.10
D	29.1-31.5	-CH (EPP+PPE), $\gamma\gamma$, $\gamma\delta$, $\delta\delta$ (EPP+PPE, PEEP, PEEE), (EEE)n	1.95-2.09
E	28-29.5	-CH(PPP)	0
F	27-28	$\beta\gamma$ (EPPE+EEPE, PPEE+EEPP)	1.86-2.11
G	24-25	$\beta\beta$ (PPEPP, PPEPE, EPEPE)	0.47-0.51
H	19-22	-CH3 (EPE+EPP+PPE+PEP)	2.32-2.55

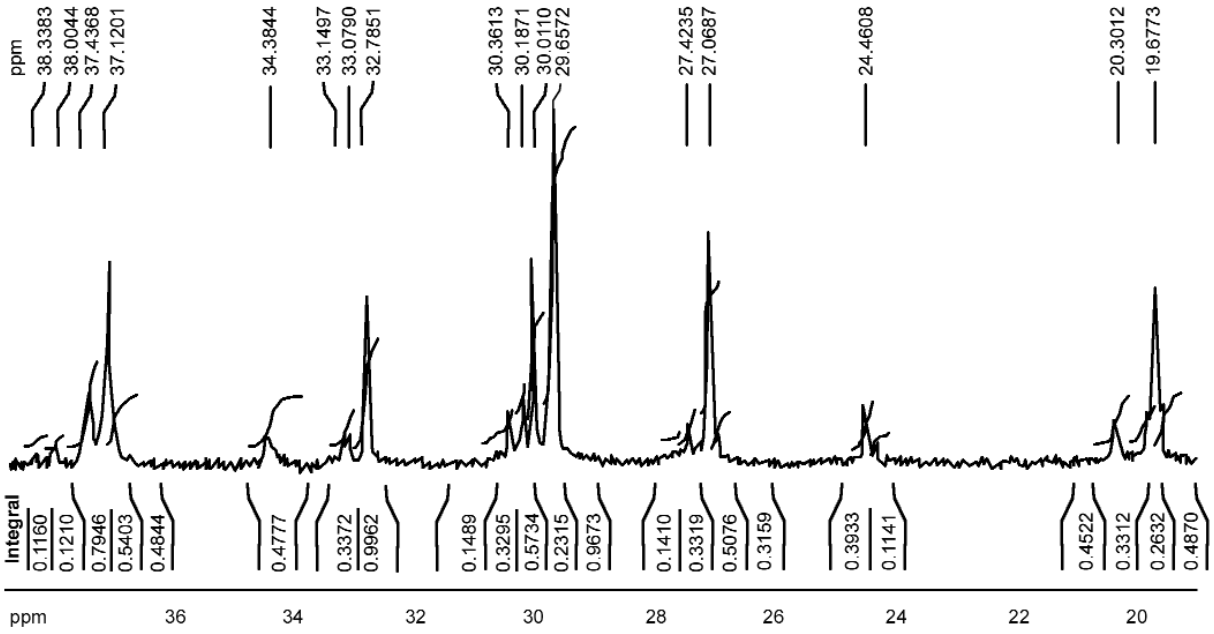

Figure 7. A ^{13}C NMR spectrum of synthesized olefin copolymer at the experimental conditions given in Table 1.

EEE and PPP triads are zero, which reduces crystalline content, and increases shear stability of the product. As indicated in Table 2, the integral intensity shows its highest values in the regions of B, H, F, D, and C which are generated by more random microstructures.

VI Behaviours

It was noticed during the course of this work that all the synthesized OCPs exhibited adequate thickening efficiency and VI values owing to their moderate molecular weight and ethylene content. But copolymer chain scission against applied shear is more than the standard criterion of the shear stability. Standard shear stability of VM is less than 12% decay in kinematic viscosity at 100°C. This failure means that copolymer chains need narrower molecular weight dispersity and more randomness in microstructure.

After many synthesis and characterization of OCP as VII, the optimum conditions were determined based on the kinetic data and structure performance relationships, to produce the finished lubricant which conform to a given specification. Viscosity index and shear stability were measured for copolymer solutions in oil as indicated in Table 3. The results from shear stability tests on fully formulated oils indicate that the copolymer is suitable as VI improvers in engine oils. A narrow molecular weight distribution was observed for the synthesized olefin copolymer as shown in Figure 5 and it was determined by gel permeation chromatography (PDI ~ 1.8).

Physical and Thermodynamic Properties

Physical properties of OCP synthesized at optimum conditions (i.e., amount of residual impurities, heat capacity, and crystalline content) were specified.

Elemental analysis on ash content indicates that

Table 3. Viscosity index and shear stability of the synthesized OCP for polymer solutions in oil.

Test	Method	Limit	Result*
Kin.viscosity at 40°C (cSt)	D 445		135.59
Kin.viscosity at 100°C (cSt)	D 445		17.58
Viscosity index	D 2270	>120	123
Shear stability	D 3945		
Kin.viscosity at 100°C (cSt)			
Before test			17.58
After test			15.52
Loss (%)		<12	11.7

(*) 1.5 wt% of polymer used in the oil formulation.

Table 4. Thermodynamic specifications of the studied olefin copolymerization system.

Olefin copolymerization	
Reaction Temp. (°C)	22
r_1	19.2-23.7
r_2	0.007-0.014
$r_1 \times r_2$	0.14-0.33
$-\Delta H$ (KJ/g)	1.0467
$-\Delta S$ (J/g.K)	3.5463

there are negligible amounts of the residual catalyst (0.02% vanadium, 0.01% aluminium and 0.05% chlorine) in OCP. The percentage of crystalline content is estimated by XRD to be less than 9 wt%. The heat capacity of the product, enthalpy, and entropy of copolymerization were calculated for this isothermal reaction by using DSC output, which are given in Table 4 with monomer reactivity ratios. The reactivity ratios are estimated by two separate methods and both of these techniques have given the same values with negligible difference. In the first method, r_1 and r_2 were obtained by the relation between monomer feed composition in the reaction medium and copolymer composition (^{13}C NMR results) as described in literature [22, 23]. In the second method, the kinetic rate constants of the propagation step have been used to calculate r_1 and r_2. They are optimized constants of the proposed dynamic model based on double moment balance method on the copolymerization [27].

CONCLUSION

The microstructure of olefin copolymers was studied to clarify their variation during ethylene-propylene copolymerization by using vanadium based soluble Ziegler-Natta catalyst in a semibatch reactor. Based on these studies, olefin copolymer was synthesized in optimum conditions. It is qualified as a suitable viscosity modifier because of its random microstructure, low crystalline content, suitable molecular weight, and narrow polydispersity. The final OCP exhibits good viscosity improving effect and shear stability behaviour at low concentration in motor oil formulation. Also, the thermodynamic specifications and physical properties of ultimate OCP of olefin copolymerization are determined.

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