

Correlation of Arrhenius Parameters for UHMWPE Synthesis with Ethylene Solubility Characteristics in Different Polymerization Media

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Received 8 October 2010; accepted 10 January 2011

DOI 10.1002/app.34137

Published online 27 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The effect of different polymerization media like *n*-hexane, cyclohexane, isooctane, *n*-decane, toluene, varsol, and light normal paraffin (LNP) on the kinetics of the slurry polymerization of ethylene using a highly active Ziegler Natta (ZN) catalyst for synthesizing UHMWPE was studied. Attempts have been made to determine the solubility of ethylene in the above polymerization media in a very basic manner and to correlate same with the process activation energy based on the Arrhenius plots. The ethylene solubility seemed to depend on the number of carbon atoms in the media, besides other parameters like geometry, dipole moment, etc. It is obvious and well understood that the monomer (ethylene) concentration has a direct bearing on the polymerization kinetics, which influenced the activation energy (E_a) besides other parameters like catalyst/cocatalyst concentration, temperature, etc which were kept constant during the study. The role of the catalyst system in

controlling the activation energy was also further exemplified by employing a different ZN catalyst system wherein higher activation energy was observed. This was ascribed to restricted activation pathways for the catalyst under the comparable experimental conditions employed. As soon as better activation pathways for the catalyst were enabled the activation energy dropped down remarkably. The E_a for the synthesis of ultra-high molecular weight polyethylene (UHMWPE) using traditional $MgCl_2$ supported Ti catalyst was found to be 5–12 kcal/mol which compared well with the values obtained by other researchers using other similar catalyst systems for different ethylene polymerization processes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2646–2652, 2011

Key words: activation energy; catalysts; kinetics (polym.); polyethylene (PE); Ziegler-Natta polymerization

INTRODUCTION

The origin of ethylene polymerization and the rigorous efforts to understand the kinetics date back to the 1930s.¹ As on date the subject area has witnessed phenomenal changes in terms of catalytic systems and processes. Extensive and commendable research has led to industrial processes for different types of polyethylene, such as HDPE (high density polyethylene), LDPE (low density polyethylene), LLDPE (linear low density polyethylene), UHMWPE (ultra-high molecular weight polyethylene), and various other speciality copolymers.^{2–10} Catalyst systems span from the traditional ZN catalysts to the present generation metallocene, single-site nonmetallocene catalysts through numerous inorganic oxide supported transition metals.^{11–17} The same is true as regards the activators or

cocatalysts, where aluminum alkyls still continue to dominate the scenario.¹⁸ Today we have homogeneous as well as heterogeneous polymerization catalysis. Despite the availability of novel well-defined homogeneous catalysts, the heterogeneous catalysts dominate the area of ethylene polymerization in the commercial scale because of the resultant product properties and lower production costs.

The exorbitant literature in the area of olefin polymerization clearly demonstrate the efforts put on to understand in totality the kinetics of the numerous processes (homogeneous and heterogeneous) possible through different permutations and combinations arising from the catalyst, cocatalyst, polymerization media, etc.^{19–21} It is quite challenging in attempting to rationalize and predict the differences in activity of the different catalyst formulations. This is mainly due to the problems in obtaining and interpreting kinetic data for the polymerization reactions, which may be extremely rapid and complex.^{22–26} The catalyst steady-state activity values can be obtained relatively easily, despite their dependence on the variable contribution of activation and deactivation

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processes.²⁷ Therefore, the rate constants for the propagation steps are not easily determined. The reaction involved multiple equilibria involving active sites as well as changes in the number of participating centers resulting in additional complications, which can influence the activity of the catalyst besides the properties of the polymer produced.

Despite the above said hurdles, eminent researchers have dealt with the kinetic aspects of certain ethylene polymerization systems.^{28–32} Extensive attempts have been made in generating as well as simulating kinetic data through modeling for different ethylene polymerization processes for better understanding. The work described here tries to estimate, understand, and correlate the effect of the solubility of ethylene monomer in different process solvents, and how it impacted the polymerization leading to UHMWPE based on the Arrhenius activation energy for a typical ZN catalyst system comprising of Ti supported on magnesium chloride.

We have been working on the synthesis of UHMWPE using traditional ZN catalyst systems and trying to understand the implications of process parameters on polymer characteristics.³³ Our elegant approach to regulate the molecular weight of UHMWPE through controlled catalyst dosing involved the study of the solubility of ethylene, hydrogen and their mixture in polymerization media under process conditions.^{34,35} We tried to understand and rationalize our observations to the industrial logic of processes switching over to hexane as the polymerization medium from other higher boiling media like varsol, decane, etc, for making UHMWPE. The prime reason is the improved kinetics, which makes the process more economical besides the elimination of energy intensive steps involved in solvent recovery and polymer drying. High boiling media like varsol, decane, etc, used for polymerization had a distinct advantage namely process safety.

Hence, it was our objective to estimate the Arrhenius parameters, mainly energy of activation, for the synthesis of UHMWPE through ethylene polymerization in different polymerization media and subsequently make an attempt to correlate the same with the solubility of ethylene in those media. We also wanted to confirm the fact that catalyst activation during polymerization is media dependant, and thus, media like toluene may not be suitable for typical ZN catalyst systems though they may have moderate to good solubility characteristics for ethylene. But toluene worked as the preferred solvent for metallocene and single site catalyst based systems since the catalyst activation pathways for such catalyst systems was favored.^{29,31,36,37}

The efficiency of the catalyst system in reducing the activation energy was also further exemplified by employing a different ZN catalyst system wherein we

observed higher activation energy due to restricted activation pathways for the catalyst under the comparable experimental conditions employed. As soon as better activation pathways for the catalyst were enabled the activation energy dropped down remarkably.

EXPERIMENTAL SECTION

Materials and methods

Varsol was the commercial sample obtained from olefin polymerization plants and was dried over molecular sieves (KC Perlen, Engelhard) before use. One of the ZN catalysts (designated A) was synthesized in the laboratory from magnesium ethoxide and titanium tetrachloride and activated using a mixture of TIBA (triisobutyl aluminum) and IPRA (isoprenyl aluminum). The other ZN catalyst (designated B) was also prepared similarly except it was having diisobutyl phthalate as the internal donor. Ethylene was used as it is from the incoming line of the olefin polymerization plant, thus avoiding further purification and drying steps. Dry and pure nitrogen gas and hydrogen gas of high purity grade was used directly from the cylinders. Other solvents like *n*-hexane, cyclohexane, *n*-decane, isooctane, and toluene were distilled over sodium hydride (NaH) and stored over activated molecular sieves for minimum moisture content (typically <10 ppm).

General experimental techniques

All glass wares were thoroughly oven dried and cooled under an atmosphere of dry nitrogen before an experiment. All manipulations like handling and transfer of catalysts and pyrophoric aluminum alkyls were carried out in a nitrogen glove bag or glove box. Safety-wares were used while handling corrosive and toxic materials like aluminum alkyls, catalyst slurries, and solvents.

Ethylene polymerizations were carried out in a 1 L Buchi Glasuster Polyclave reactor fitted with magnetically driven agitator. The reactor was made oxygen and moisture free before carrying out the polymerization. It was connected to a cryogenic system to maintain the desired temperature in the reactor. All manipulations were carried out under N₂ and moisture free atmosphere while carrying out the polymerizations.

Experiments pertaining to ethylene solubility in different polymerization media

For correlating the activation energy with ethylene solubility in different polymerization media employed, we have determined the solubility of ethylene in those

media. The experiments were conducted at 30°C and in a fixed volume of the medium (500 mL) in the 1 L Buchi Glasuster Polyclave itself. Ethylene gas was allowed to dissolve until saturation in the medium under a constant agitation speed (500 rpm). Subsequently the dissolved gas was vented out under stirring through a gas flow meter which measured the amount of gas. The capped gas, i.e., headspace gas above the liquid level was same throughout in all the runs, and hence, it was not considered in the calculations. This was measured at different pressures up to a maximum of 2.5 bar. We observed the dissolved gas to increase in volume as per Henry's law. We found this to be an elegant way of measuring the solubility of gases in liquids in a straight forward manner. The trend observed was matching based on the values reported in NIST data base.³⁸ We assumed the same trend to follow suit at higher temperatures wherein the polymerizations would be performed.

Polymerization experiments pertaining to Arrhenius parameters

A typical polymerization experiment to determine the E_a from the Arrhenius plot was carried out employing 500 mL of varsol. To that was added a solution of a cocatalyst comprising of an equal mixture (v/v) of TIBA and IPRA diluted in varsol and having a concentration of 20% (w/v). The catalyst slurry in hexane was homogenized to get a uniform concentration and a suitable amount was transferred out for each run such that the Al/Ti was around 4. The exact quantity of the catalyst slurry to be transferred was ascertained from its slurry concentration and Ti content. The molar ratio of the activator (Al from aluminum alkyl) and the catalyst (Ti from catalyst) was maintained around 4 (Al/Ti) for all the runs. After boxing up the reactor, the occluded gas in the medium was vented out gently under agitation. After stopping the agitator, ethylene was then introduced into the system at desired pressure (2.5 bar). Polymerization was performed at desired temperature under agitation (500 rpm) and ethylene pressure was maintained at 2.5 bar through out the run (1 h). Simultaneously the heating and cryogenic facilities were started and the temperature was maintained as required for the Arrhenius run by controlling the exothermic nature of the polymerization. After 1 h the residual ethylene was vented out and the contents of the reactor discharged into a receiving vessel after cooling the reactor and contents to ambient temperature. The polymer formed was in the form of uniform powder. The polymer was filtered and dried under vacuum at 75°C. The amount of polymer obtained was used to compute the rate for each Arrhenius run carried out at designated temperature under identical conditions.

Polymerization runs employing other media like *n*-hexane, cyclohexane, etc, were performed exactly as described above except by using the concerned medium in place of varsol. For estimating the activation energy (E_a) for the process in different polymerization media, the polymerizations were conducted at 4 to 5 different temperatures in each medium keeping all other process conditions same. The amount of polymer obtained formed the basis for computing the rate. A logarithmic plot of rate versus the reciprocal of the corresponding temperature yielded a straight line. Multiplication of the slope of this line with 1.987 gave the E_a .³¹

RESULTS AND DISCUSSION

Solubility of ethylene in different process solvents used for polymerization

One of the crucial factors controlling the kinetics of olefin polymerization is undoubtedly the concentration of the olefin as governed primarily by its solubility in the medium under the polymerization conditions employed. This dependency of the polymerization kinetics on the medium employed will largely influence the characteristics of the polymer synthesized. The polymerization medium also partly holds the key toward catalyst activation pathways, which will also dictate the kinetics. Without entering into the complicated realms of polymerization kinetics the present work is mainly restricted in evaluating the solubility of ethylene in different media at ambient temperature and pressure in a simple, practical, and elegant manner. This solubility data in the form of Henry's constant was subsequently used to correlate and establish the existence of any link with the process activation energy for UHMWPE synthesis as determined through Arrhenius plots.

The solubility of ethylene in different polymerization media was determined over a pressure range of 0.5 to 4 bar at constant temperature (30°C) and fixed solvent volume (500 mL) in the Buchi polyclave reactor. The plot of dissolved ethylene versus applied pressure resulted in a straight line obeying Henry's law of solubility as shown in Figure 1. The slope of the line represented Henry's constant for each determination in the specified medium under the experimental conditions employed (Table I). We have extrapolated these results to higher temperatures like 40 to 80°C and assumed that the solubility trend will remain same in the different polymerization media. This was necessary since the polymerizations were carried out in the temperature range of 40 to 80°C for determining the E_a from the corresponding Arrhenius plots.

The solubility of ethylene depended on the nature of the medium, namely its size, shape, physical, and

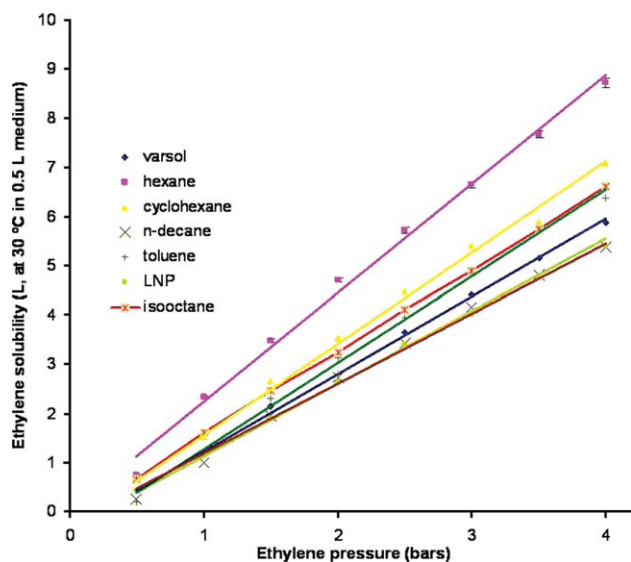


Figure 1 Solubility of ethylene in different polymerization media at different pressures (All the trend lines conform to an R^2 value close to 1 indicating more than 95% confidence limit). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemical constants, etc. The solubility decreased as the carbon number of the alkane increased. Thus, the solubility of ethylene was less in *n*-decane as compared with *n*-hexane. The solubility decreased in cycloalkanes (as seen from cyclohexane) compared with linear alkanes (*n*-hexane). The solubility was moderate in aromatic solvents like toluene. Solvents like varsol and LNP comprised of a mixture of alkanes and their isomers, with *n*-nonane and *n*-decane as the major constituents. The solubility of ethylene in such solvents was also in order as observed for the other alkanes and isoalkanes.

Catalyst activation pathways in different process solvents used for polymerization

Olefin polymerization mediated by ZN catalysts proceeded through an important step of catalyst activation in the said medium facilitated by aluminum alkyl as the activator under the process conditions used. The catalyst activation pathway led to generation of a coordinative unsaturated site on the metal

TABLE I
The Ethylene Solubility in Different Polymerization Media at 30°C

Medium	Ethylene solubility (L/bar, Henry's constant)
<i>n</i> -hexane	2.2221
Cyclohexane	1.7478
Toluene	1.585
Varsol	1.4508
<i>n</i> -decane	1.351
LNP	1.3371

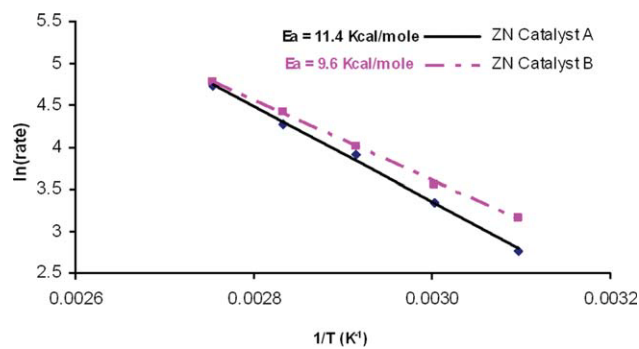


Figure 2 Dependency of E_a over catalyst nature in varsol as medium. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

center (Ti in our case) of the ZN catalyst. Monomer coordination took place on this site followed by polymerization through chain propagation and termination steps. The efficiency of the catalyst activation pathway in the medium would also have a direct implication on the polymerization kinetics and the Arrhenius activation energy. Although ZN catalyst (A) was effective for synthesizing UHMWPE in *n*-alkanes, isoalkanes, and cycloalkanes to different extents as judged from E_a ranging from 5 to 14 Kcal/mol, it was ineffective in toluene as the medium.³¹ The electronic environment in the aromatic solvent definitely inhibited the catalyst activation under the experimental conditions employed. To authenticate this, the experiment was performed under higher ethylene pressure of 7.5 bar and the polymerization could be initiated since the catalyst activation pathway was enabled to an extent. No further attempts were made to determine the E_a for the process in this medium since that will require major departures in the polymerization conditions and thus preventing a scientific comparison. The experiment was restricted only to the measurement of ethylene solubility in toluene under comparable conditions. Toluene was the preferred solvent for homogeneous and single site catalyst systems of the metallocene and non metallocene types.^{29,31,36,37}

The difference in catalyst activation behavior of the two ZN catalysts, (A) and (B), for the synthesis of UHMWPE under identical conditions in varsol resulted in E_a of 11.4 Kcal/mol for the former and 9.6 Kcal/mol for the latter (Fig. 2). This experiment signified that the monomer solubility and catalyst activation in the polymerization medium complement each other.

Arrhenius energy of activation for UHMWPE synthesis in different process solvents used for polymerization using ZN catalyst (A)

The logic behind industrial processes switching over to hexane as a polymerization medium from higher

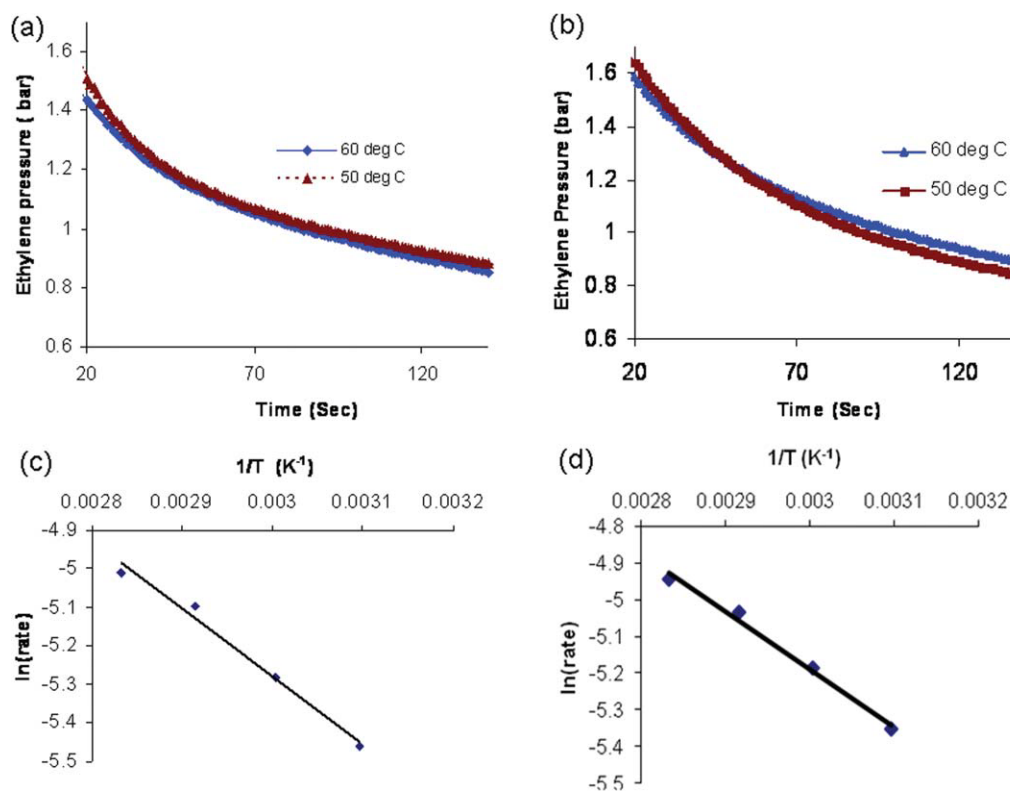


Figure 3 Plot of ethylene pressure vs time in (a) *n*-hexane, (b) cyclohexane; Arrhenius plot of initial rate in, (c) *n*-decane, (d) varsol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

boiling medium like varsol had to be comprehended scientifically besides the known better process economics utilizing less energy. The straight forward scientific rationale was to determine the energy of activation from Arrhenius plots for the synthesis of UHMWPE in the different polymerization media. This will reflect the energy barrier the process had to overcome in each media. Because all the parameters were maintained constant excluding the polymerization medium, the results should reflect the effect of the monomer solubility in the respective medium along with the catalyst activation pathway.

Toluene was the only medium which was significantly different from the others. Hence, it would not be improper to assume that the catalyst activation pathway contribution toward the Arrhenius activation energy would be roughly same for the other media comprising of alkanes, isoalkanes, and cycloalkanes. To ascertain and authenticate this, the initial rates of polymerization in those media were determined at temperature ranges between 50 to 80°C so as to arrive at the Arrhenius E_a through a plot of the logarithmic rate against the reciprocal of the absolute temperature. The polymerization at the designated temperature was initiated and the drop in ethylene pressure from the set pressure of 2 bar was monitored every second for about 5 to 10 min by which time the rate had started to stabilize. For lower boiling solvents like *n*-hexane and cyclohexane

the upper temperature limit was kept 60°C to prevent interference from the vapor pressure of the solvent. In such cases the initial rates were studied only at two temperatures, and hence, the Arrhenius plot was not done. The Arrhenius E_a was directly calculated from the Arrhenius equation itself. The time interval used for calculating the rates from the Arrhenius plot or from the equation was kept constant, namely 20 to 140 s since we found that to be the correct time interval for taking the tangential slope for initial rate measurement. The Arrhenius E_a during the initialization of the polymerization as computed for *n*-hexane, *n*-decane, cyclohexane, and varsol was roughly same and ranged between 3.5 ± 0.1 kcal/mol (Fig. 3). This provided the evidence that the catalyst activation pathway was roughly same in those media and was independent of the monomer solubility in the media.

The overall reaction rates were determined subsequently to understand the impact of the catalyst activation pathway as well as the monomer solubility on the Arrhenius E_a for the polymerization process.³¹ These determinations were done by maintaining a constant monomer pressure of two bars through out the polymerization and at other fixed conditions described at appropriate places. The results obtained for the estimation of the overall Arrhenius activation energy in the various polymerization media excluding toluene are given in Figure 4.

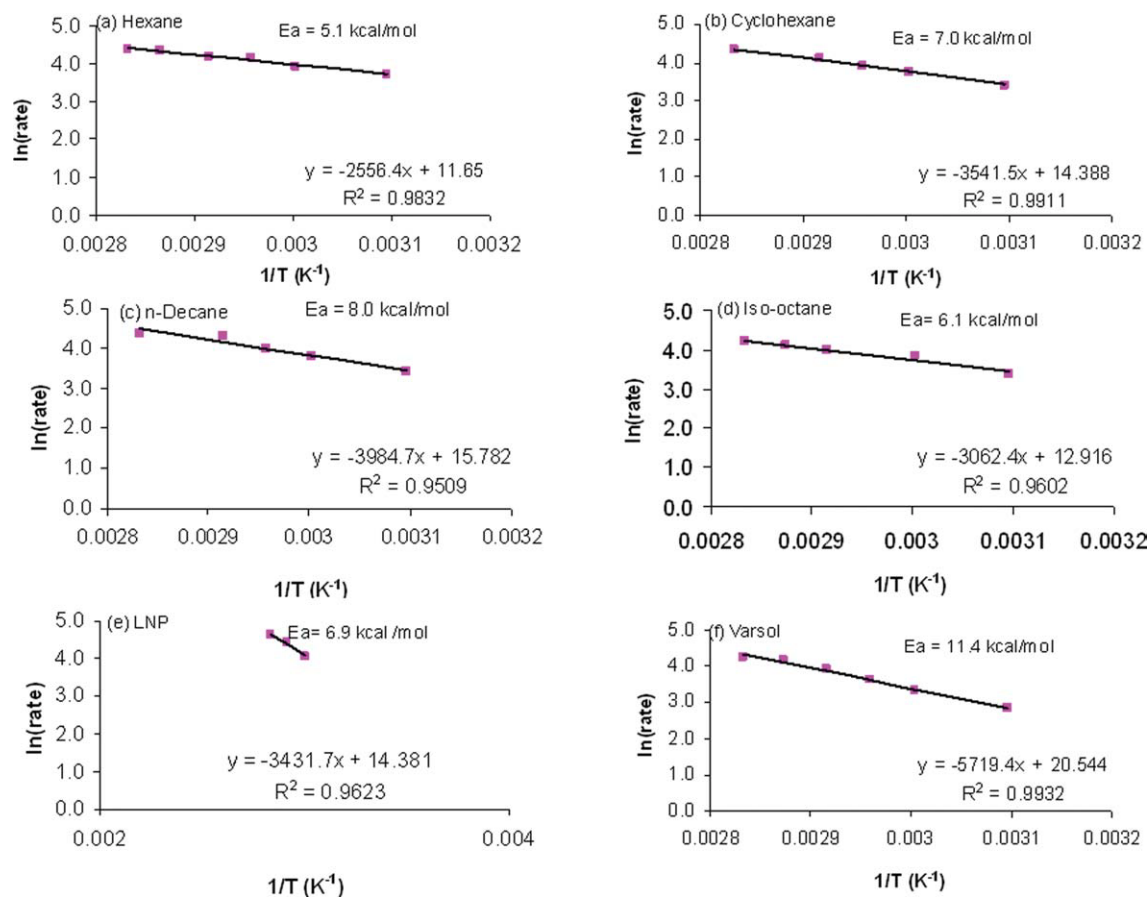


Figure 4 E_a for UHMWPE synthesis in different polymerization media. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We observed that *n*-hexane had the least E_a and varsol the maximum. The E_a in the other *n*-alkanes, cycloalkane, and isoalkane was ranging from 6 to 8 Kcal/mol which was in agreement with literature reported well defined catalyst systems.^{37,39,40}

The impact of the monomer solubility (as estimated from the Henry's constants) on the overall Arrhenius E_a for the various media can be seen in

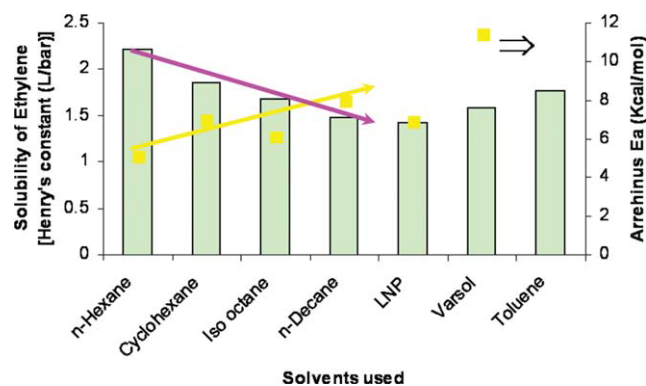


Figure 5 Correlation of E_a for UHMWPE synthesis and ethylene solubility in different polymerization media. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. The trend was very clear since E_a increased as the monomer solubility in the media decreased. The ethylene solubility further seemed to depend on the number of carbon atoms in the media, besides other parameters like geometry, dipole moment, etc. This resulted in slight difference in the absolute values of the solubility and E_a , nonetheless the trend observed was obvious. More credence should be given to the trend and not to the individual values since that would result in ambiguity in the discussion. The polymerization kinetics in each media would be different and consequently the polymer characteristics would also be impacted by this. It was precisely for such reasons that a suitable balance had to be worked out in selecting the media based on economics, process kinetics, and polymer characteristics. The Arrhenius proportionality constant, A , was found to be 100 to 150 for the different polymerization media employed in the study.

CONCLUSIONS

The solubility of ethylene in different polymerization media like *n*-hexane, cyclohexane, isooctane, *n*-decane, toluene, varsol, and light normal paraffin was

determined in an elegant manner to arrive at the Henry's constant. The ethylene solubility seemed to depend on the number of carbon atoms in the media, besides other parameters like geometry, dipole moment, etc. The Henry's constants were correlated with the overall process E_a for synthesizing UHMWPE using a highly active ZN catalyst based on the Arrhenius plots. The E_a increased as the ethylene solubility decreased in the polymerization media. The catalyst system had a role in controlling the activation energy as exemplified by employing a different ZN catalyst system, wherein higher activation energy was observed due to restricted activation pathways for the catalyst under the comparable experimental conditions employed. This signified that the monomer solubility and catalyst activation in the polymerization medium complement each other. The Arrhenius E_a during the initialization of the polymerization as computed for *n*-hexane, *n*-decane, cyclohexane, and varsol was more or less same ranging between 3.5 ± 0.1 kcal/mol indicating that the catalyst activation pathway was almost similar in those media and was independent of the monomer solubility in the media. The overall Arrhenius E_a for the process in different polymerization media was found to be 5–12 kcal/mol which compared well with the values obtained by other researchers using other catalyst systems for different ethylene polymerization processes.^{28–32}

The authors sincerely thank Dr. Ajit Mathur and Dr. Rakshvir Jasra for their continuous encouragement and support in carrying out this work.

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