Petroleum Resin Preparation by Cationic Polymerization of Pyrolysis Gasoline

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A B S T R A C T

This study investigates the process for manufacturing of petroleum resin from pyrolysis gasoline feedstock taken from Tabriz Petrochemical Company. These resins have been used extensively in a wide variety of areas such as adhesives, paint, and printing inks industries. This product is prepared through polymerizing a petroleum fraction containing unsaturated hydrocarbons with the presence of Friedel-Crafts catalyst. The resins were characterized by ^{1}H NMR and IR spectroscopy and the effective factors in the production of petroleum resins, reaction temperature, amount of catalyst and solvent types were analyzed. Analysis of the polymerization temperature demonstrates that resins with high molecular weights and softening points are produced at low temperatures. The optimal amount of catalyst to prepare resins with high molecular weight and softening point is achieved at 0.45-1.25 wt% of the feedstock. When polymerization takes place in the presence of aromatic solvents, the molecular weight and softening point of resins are reduced. The addition of compounds such as indene and styrene led to an increase in molecular weight and softening point while it reduced the resin yield dramatically. These compounds can be utilized to regulate molecular weight.

INTRODUCTION

Hydrocarbon resins have many applications [1,2]. They are seldom used alone, but mostly in conjunction with other materials to achieve specific properties [3]. These specific properties may be used to classify such resins as hard resins, mainly used in the paint and varnish industry; plasticizer and compounding agents in the plastic industry (rubber and PVC); compounding tackifying resins in adhesives [1,4]; and fixing agents in wood protection. Largely, raw materials for the manufacture of

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resins were found with development of the chemical industry in the 1940s [5]. Hydrocarbon resins can be prepared by cationic polymerization of a cracked petroleum feed containing C_4, C_5 to C_{12} paraffin, olefins, and diolefins. These monomer streams are comprised of cationically polymerizable aliphatic monomers such as butadiene, 1,3-pentadiene (piperylene) along with cyclopentene, 2-methyl-2-butene, isoprene and unsaturated aromatic monomers such as styrene, indene, vinyl toluene, cyclopentadiene, and dicyclopentadiene. In order to obtain these feeds, the refinery streams are purified usually by both fractionation and treatment to remove impurities. Manufacture of hydrocarbon resins are conventionally produced by adding $AlCl_3$ [6], BF_3 or other Friedel-Crafts acids [7] to a particular feedstock, mostly in the presence of various promoters such as HCl, t-BuCl [8], alcohol ether [9], water or phenol. Older processes use H_2SO_4 or H_3PO_4[10].

The production of hydrocarbon resins involves selection and pretreatment of raw materials, polymerization of the prepared feed, deactivation of initiating system (neutralization), and eventually the separation of resin. The most important reaction parameters are: feed composition [11], total and relative concentration of resin formers in the feed, type of initiating system and its concentration [12], temperature [13] and kinetics (isothermal or adiabatic). These parameters must be carefully controlled as they affect the reaction in terms of yield, type (polymerization, alkalization), molecular weight, and its weight distribution. Deactivation is achieved by adding a nucleophilic quenching agent to the reaction mixture in order to convert residual Friedel-Crafts acids and derivatives to conveniently disposable species. Polymerizates contain 40-50% of saturated hydrocarbons, together with a certain percentage of low molecular weight polymers (oligomers). These materials are separated by distillation. The standard vacuum distillation used to remove non-reacted materials may be followed by a steam-stripping step to drive out the remaining solvent, monomers and if present, light oligomers. Since the polymerization reaction is normally exothermic, it is usually carried out in the presence of a solvent so as to properly control the reaction rate and to prevent gel formation. In cases where there are no technical problems due to the reaction heat or gel formation, however, the reaction can be carried out in the absence of a solvent [14]. Aliphatic hydrocarbons such as hexane, heptane, and cyclohexane; aromatic hydrocarbons such as benzene, toluene and xylene; and halogenated hydrocarbons such as methylene chloride and the like are used as a solvent either independently or mixed with one or more others. There is no specific restriction as to the type of polymerization reaction employed. It may be carried out either batchwise, semi-batchwise, or continuously [15]. In this study we investigated the process for manufacturing petroleum resin from pyrolysis gasoline feedstock taken from Tabriz Petrochemical Company for industrial usages.

EXPERIMENTAL

Materials and Instruments

Pyrolysis gasoline V-151 obtained from Tabriz Petrochemical Company (Table 2), anhydrous $AlCl_3$(Fluka, 133.34, France), boron trifluoride, sodium hydroxide, were purchased from Merck and used without purification. Toluene anhydride was dried with Na before use.

^{1}H NMR Spectra were carried out on a Bruker Avence 400 spectrometer. The spectra were recorded in the 4000-400 cm^{-1} range from a Fourier transform Shimadzu 7R-40E spectrometer. IR Spectra were obtained using a Shimadzu IR-405 spectrometer. GC was carried out on a Chrompack -cp-9001 instrument with a flame ionization detector. GPC Measurements were carried out on a Waters apparatus fitted with Wlterstyragel columns (10^4 A°, 10^5 A°, 10^6 A°). The elution solvent was DMF or THF, with the flow rate 2.0 mL/min and IR detector. With respect to the hydrocarbon resin, the physical properties, the resin yield, viscosity (ASTM D4307-88) [16], to measure softening point, we employed Ring & Ball Method (ASTM D 36-86) [17].

Procedure

One gram of anhydrous $AlCl_3$ as a catalyst along with 5 mL of toluene anhydrous were placed in a 1 L glass reactor in order to make a suspension of the solvent and catalyst. Then, the reaction suspension was exposed to N_2 gas with a specified flow. The reaction takes place in a neutral condition because oxygen here can act as a terminating agent. Then to the above suspension, 120 g of feedstock was added in droplets by dropping funnel

Table 1. The GC analysis of Tabriz Petrochemical pyrolysis gasoline.

Component	Concentration (wt %)	Component	Concentration (wt %)
IC_4	0.01	NC_7	0.04
NC_4	0.016	$M\text{-}CYCC_6$	0.11
$1,4\,C_5{==}$	0.014	$E\text{-}CYCC_5$	0.01
IC_4	1.07	$2,5DMC_6$	0.09
NC_4	1.93	$3,3DMC_6$	0.05
$1C_4{=}$	0.27	TOL	14.77
$2M1C_4{=}$	0.31	$2MC_7$	0.09
2M1,3BDN	2.04	$3MC_7$	0.02
$T\text{-}2C_5{=}$	0.07	$1C_8{=}$	0.15
$2M2C_4{=}$	0.02	NC_8	0.03
$T\text{-}1,3C_5{==}$	1.03	$2,4DMC_7$	0.01
$CYCC_5{==}$	3.75	EB	0.9
$CYCC_5{=}$	0.56	M,P-XYL	2.19
$4M1C_5{=}$	0.01	SM	14.9
$CYCC_5$	0.65	o-XYL	0.73
$2MC_5$	0.41	IPB	0.01
$3MC_5$	0.07	NPB	0.08
$2M1C_5{=}$	0.19	3E-TOL	0.23
NC_6	0.52	4E-TOL	0.10
$2M2C_5{=}$	0.12	1,3,5TMBZ	0.04
$T_2C_6{=}$	0.16	2E-TOL	0.2
$CIS\text{-}2C_6{=}$	0.09	1,2,4TM-BZ	0.16
$MCYCC_5$	0.58	NC_{10}	0.10
$4M1,3C_5{==}$	0.85	$1C_{10}{=}$	0.01
$1M1CYCC_5{=}$	0.99	1,2,3,TMBZ	0.32
BZ	45.72	DCPD+Indene	4.04
$3,3DMC_5$	0.02	DHDCPD+	1.79
$CYCC_6$	0.19	Indene	0.01
$MCYCC_5{==}$	1.06	DEB	0.06
$2MC_6$	0.03	BBZ	0.05
$2,3DMC_6$	0.01	THDCPD	0.34
$1,1DMCYCC_5$	0.05	Naphthalene	0.08
$CYCC_6{=}$	0.17	NC_{12}	0.16
$CIS1,3DMCYCC_5$	0.06	1,3,5TEBZ	0.01
$T\text{-}1,3DMCYCC_5$	0.04	2-Methylnaphthalene	BALANCE
$T\text{-}1,2DMCYCC_5$	0.08	OTHER,S	

over a period of 30 min. The reaction suspension was stirred at a constant speed. Because the polymerization reaction was exothermic, the polymerization heat was controlled to keep temperature at 25°C. Meanwhile, the reflux state is maintained. Right after the addition of feedstock into suspension, the reaction starts. The whole reactive process takes place in 90 min. Next, 40 mL of a 20 wt% of sodium hydroxide aqueous solution was added to the reaction suspension to finish the polymerization reaction.

Then, these materials were taken into a glass decanter and washed with 300 mL distilled water three times in order to remove the remaining catalyst. The upper phase was transferred to a clean glass flask and was distilled under vacuum at a temperature of 180°C for 2 h with the purpose of removing solvent and low molecular weight oligomers. After the completion of this stage, melted resin is taken out of the flask and is left to cool gradually. Then, the final product is weighed.

RESULTS AND DISCUSSION

Polymerization with $AlCl_3$ catalyst takes place in the presence of a little water as a co-catalyst. In so doing, a little water causes aluminium chloride to become hydrolyzed and consequently a complex acid is produced. For example, considering one of the monomers in the feedstock, we can write:

$$(AlCl_3OH^-)H^+ \; + \; CH_2{=}\underset{\underset{C_6H_6}{|}}{CH} \longrightarrow$$

$$\underset{\underset{C_6H_6}{|}}{CH_3CH^+} \; + \; (AlCl_3OH^-) \qquad (1)$$

Carbonium ion can affect other monomers and result in polymerization. As a matter of fact, the propagation is a rather complex step and very difficult to achieve. Next, growing carbonium ions are transferred to another chain or monomer (M). Such transfer depends on the ability of the monomer as well, and it may happen by direct or indirect chain growth.

In the direct mode:

$$\text{(chain)} \; C^+ \; + \; M \longrightarrow \tag{2}$$

$$[\text{transition state}] \longrightarrow \text{(chain)} \; C^* + HM^+$$

Or, indirectly through the intervention of a nucleophilic transfer agent:

$$\text{(chain)} \; C^+ \; + \; Nu \xrightarrow{\;M\;} \tag{3}$$

$$[\text{transition state}] \longrightarrow \text{(chain)} \; C^* \; + \; {}^-M^+$$

Where:

C^+: is the growing carbonium ion;

C^*: the cyclic olefin units, or non-propagating -CH;

Nu: a charged or neutral nucleophilic transfer agent; and

M^+: the new cationic monomer chain carrier.

The most remarkable step in this process is the generation of a new propagating unit. Termination results in the irreversible destruction of the propagating kinetic chain. It should be noted that chain transfer and termination are quite different processes and need to be carefully distinguished from one another. Termination reactions may occur in different forms. This is done by the introduction of a neutral nucleophile:

$$\text{(chain)} \; C^+ \; + \; Nu^+ \longrightarrow \tag{4}$$

$$\text{(chain)} \; CNu$$
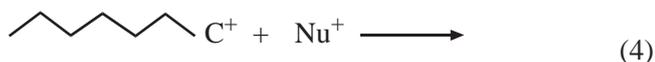
Alcohols [6], ammonia, amines, alkalis [14], or simply
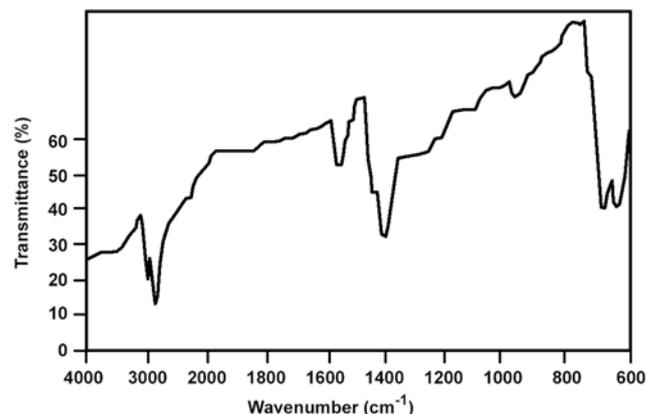
Figure1. IR Spectrum of obtained resin. Resin was prepared at 25°C temperature in 5 mL toluene.

water [11] can be used as nucleophiles. It is obvious that obtaining precise data concerning resins made of a complex mixture is very difficult.

Figure 1 shows an IR spectrum of the synthesized resin. The main objective behind IR spectrum analysis is to identify functional groups. Moreover, such analysis allows us to identify the resin types, i.e. aromatic, aliphatic or their mixture. Aromatic resins are characterized by a weak absorption at 3040 cm^{-1}, together with absorption between 1600 and 1500 cm^{-1} and under 900 cm^{-1}. The emerged absorption at 3040 cm^{-1} is due to the stretching vibrations in aromatic compounds (=C-H). Likewise, aliphatic resins are characterized by absorption at 2900 cm^{-1} along with weak absorptions at 1600-1680 cm^{-1} and 1450 cm^{-1}. Absorption frequency at 2900 cm^{-1} is because of stretching vibrations (-CH in alkenes). The (C=C) bond in aliphatic compounds gave a weak absorption frequency at

Table 2. The effect of amount of AlCl$_3$ catalyst on some properties of resins.

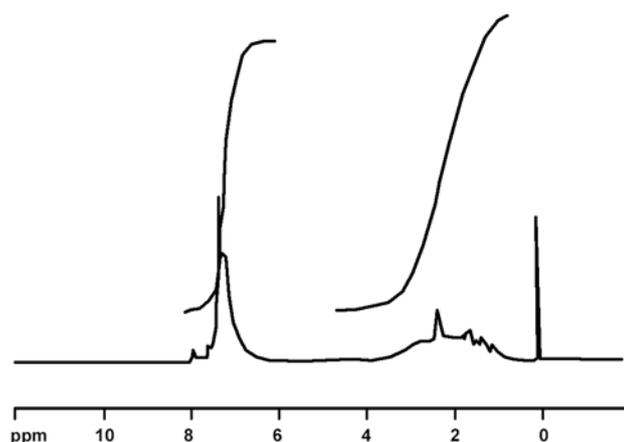| Sample	Concentration catalyst (g)	Softening point (°C)	Resin viscosity (Ps)	Resin yield (g)	Number average molecular weight (Dalton)	Weight average molecular weight (Dalton)	Polydispersity (PDI)
1	0.5	71	1.327	35	1088	1315	1.2
2	0.7	75	1.39	55	1546	2416	1.56
3	1	76	1.52	60	1548	2491	1.6
4	1.5	73	1.636	68	1062	1250	1.17
5	2	73	1.314	70	1015	1161	1.15

Reaction temperature 25(°C) and toluene 5 mL.

Figure 2. ^{1}H NMR spectrum of obtained resin. Resin was prepared at 25°C temperature in 5 mL toluene.

Figure 3. Effect of amount of catalyst on number average molecular weight distribution.

1600-1666 cm^{-1}. IR Spectrum illustrates that synthesized resin is a mixture of aliphatic and aromatic.

One of the most useful and quickest methods to identify resins is by proton nuclear magnetic resonance spectroscopy known as ^{1}H NMR (Figure 2). Aliphatic protons give peaks in the region 0-2 ppm, and aromatic protons in the region 7 ppm. The proportion of aromatic to aliphatic proton is useful in classifying resins and finding their applications. The proportion of aliphatic protons to aromatic protons in our synthetic resins is 1.1:0.9. The emerged peaks in the region 2-3 ppm are due to the resonance of carbon protons attached to a double bond in the resin structure. Thus, the presence of double bond aliphatic compounds is definite.

Figure 3 shows the amount of consumed catalyst on number average molecular weight distribution. During polymerization, the amount of catalyst may vary from 3 to 25 wt% of the polymerizable compounds in the feedstock and that is why the reaction was carried out in different amounts of the catalyst in our study. For aluminium chlorides less than 0.41 wt% (0.5 g), polymerization reaction did not start at all. A large amount of catalyst, that is, 1.25 wt% (1.5 g) did not have a major impact on the molecular weight. It should also be kept in mind that using a large amount of the catalyst is not economically cost-effective. To synthesize industrial resins, we found the optimal amount of the catalyst in our study ranging from .58 to 1.5 wt% of the feedstock.

According to Figure 4, the maximum softening point of resin is obtained at about 0.7 to 1.5 g of catalyst. The softening point depends on the structure of the resin. An increase in catalyst concentration induces a rise in resin yield (Figure 5). This is due to the fact that Lewis acids are mostly in the form of dimer and the solvent is not capable of breaking all dimers. As a result, some of the catalyst remains dimer and inactive in the reaction. In addition, we know that an excessive

Table 3. The effect of catalyst types on some properties of resins.

Sample	Catalyst	Concentration (g)	Softening point (°C)	Resin viscosity (Ps)	Resin yield (g)	Number average molecular weight (Dalton)	Weight average molecular weight (Dalton)	Polydispersity (PDI)
1	AlCl$_3$	0.5	71	1.327	35	1088	1315	1.2
2	AlCl$_3$	0.7	75	1.39	55	1546	2416	1.56
3	BF$_3$	0.5	122	1.897	65	1355	1538	1.13
4	BF$_3$	0.7	128	1.930	69	1654	1986	1.2

Reaction temperature 25(°C) and toluene 5 mL.

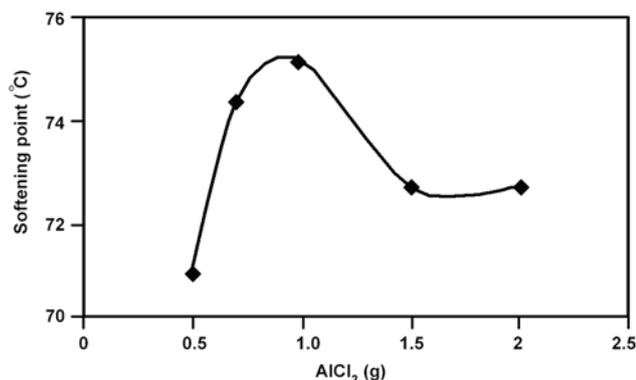Figure 4. Effect of amount of catalyst on resin softening point.

Figure 5. Effect of catalyst on resin yield.

increase of the catalyst has no effect on the molecular weight, so we choose an optimal amount of the catalyst which raises molecular weight, softening point, and resin yield. Resins prepared in the presence of BF_3 enjoyed higher molecular weight, softening point and resin yield in comparison with the ones produced in the presence of $AlCl_3$ catalyst. The findings on polymerization with both catalysts are illustrated in Table 4. According to these findings, we can conclude that catalyst activity can play a significant role in the polymerization reaction and resin features. The following mechanism is suggested for polymerization in the presence of BF_3 [21] :

$$BF_3 + H_2O \longrightarrow (BF_3OH^-)\, H^+ \qquad (5)$$

Following this, the effect of the temperature on polymerization was investigated. Temperature is the most important parameter in controlling molecular weight.

As illustrated in Figure 6, the higher the temperature, the lower the molecular weight of the synthesized resins. Regarding the kinetic cationic polymerization by

Lewis acids, these finding are quite expected. Molecular weight is in reverse proportion with temperature. As temperature drops, the active centres which are formed are not destroyed. Consequently, the propagating reactions overcome termination and then the chain growth increases. However, when temperature increases, the required energy to terminate the chains is supplied, and thus the terminating stage happens sooner. Eventually, there will be resins with low molecular weight.

The most outstanding factor which leads to the hardness and brittleness of resins is the softening point. Resin softening point is reduced as temperature is raised (Figure 7), that is to say, the softening point of the resin is influenced by its structure. If the prepared resin is harder, the softening point will be higher as well. The resin hardness decreases in polymerization at high temperatures because the molecular weight of the polymers reduces. It also becomes easy to overcome resin structure, and thus resins melt at low temperatures. To prepare hard resins at high molecular weight, the range of temperature 0-30ºC is suggested. The reaction yield declines as the polymerization temperature goes up (Figure 8). This is due to the fact that an increase in the reaction temperature provides the

Table 4. The effect of styrene(wt%) on some properties of resins.

Polydispersity (PDI)	Weight average molecular weight (Dalton)	Number average molecular weight (Dalton)	Resin yield (g)	Softening point (ºC)	Styrene (wt%)
1.56	2416	1546	55	74	14.9
1.15	2196	1910	45	84	32.11
1.2	2390	1992	36	100	42.02

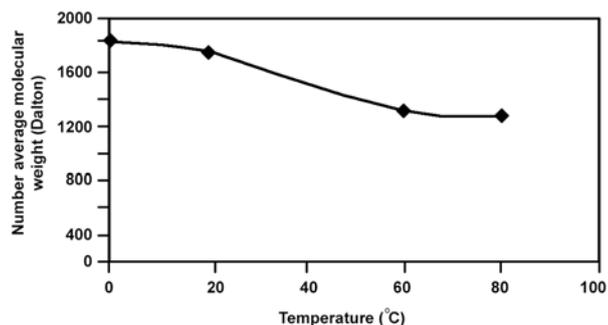Reaction temperature 25(ºC), $AlCl_3$ catalyst 0.7 g and toluene 5 mL.

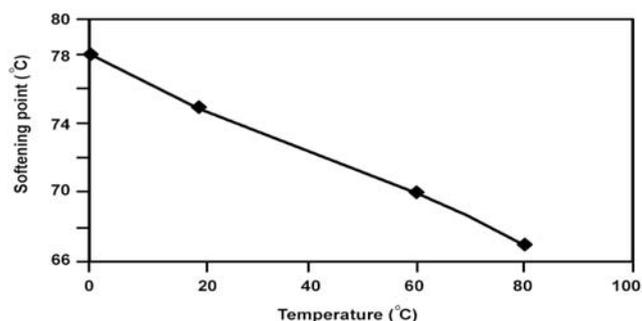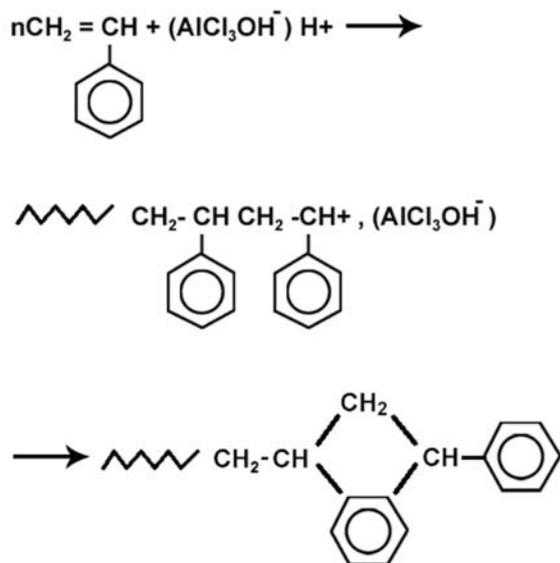**Figure 6.** Effect of reaction temperature on the number average molecular weight.

Figure 7. Effect of reaction temperature on softening point of obtained resin.
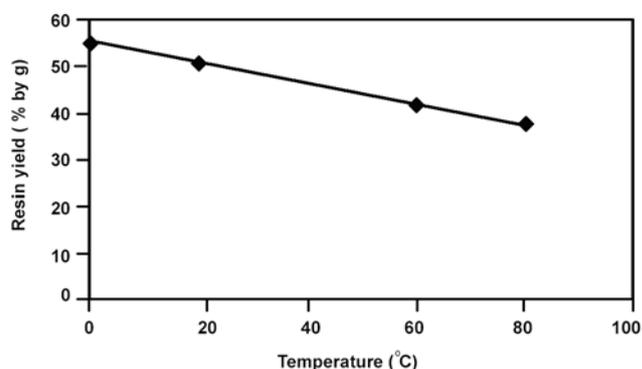
Figure 8. Effect of reaction temperature on resin yield.

required energy to terminate growing chains, and thus chains reach the terminating stage sooner. There is also a high degree of low molecular weight chains in the reaction. These chains are eliminated at distillation, so a few chains have the chance to grow considerably. This in turn reduces the ultimate resin yield.

To consider the effect of styrene on polymerization [19,20] the rate of styrene in the reaction was raised. Significant changes were observed in the softening point and molecular weight of the produced resins (Table 4). An increase in styrene led to a rise in the softening point while this reduced molecular weight in the synthesized resins. Therefore, styrene can be used to control and regulate the molecular weight. In the presence of styrene, the intramolecular reactions also take place and cause the molecular weight to decrease in the synthesized resins [21].

While boosting resin hardness, these reactions are responsible for a reduction in the molecular weight and resin yield. An amount of 4 wt% addition of indene induces considerable rise in the softening point while it reduces molecular weight and yield in the synthesized resins (Table 5). However, a 25 wt% increase in indene
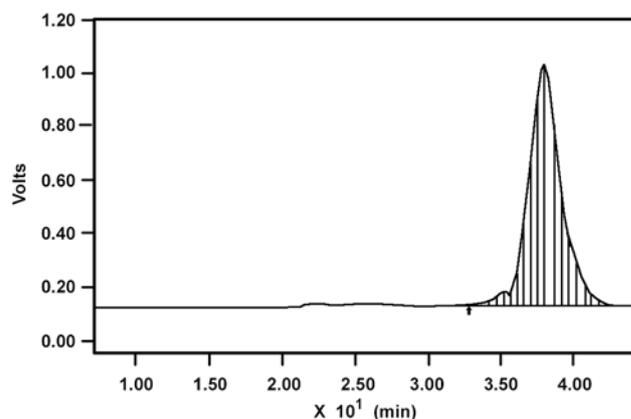

Figure 9. GPC spectrum of resin. Resin was prepared at 25°C temperature in 5 mL toluene.

Table 5. The effect of indene(wt%) on some properties of resins.

Polydispersity (PDI)	Weight average molecular weight (Dalton)	Number average molecular weight (Dalton)	Resin yield (g)	Softening point (°C)	Styrene (wt%)
1.56	2416	1546	50	74	4.04
1.2	1412	1152	36	96	27.66

Reaction temperature 25(°C), $AlCl_3$ catalyst 0.7 g and toluene 5 mL.

Table 6. Effect of solvents on some properties of resins.

Sample	Concentration BF_3 catalyst (g)	Toluene (CC)	Softening point (°C)	Resin viscosity (Ps)	Resin yield (g)	Number average molecular weight (Dalton)	Weight average molecular weight (Dalton)	Polydispersity (PDI)
1	0.5	0	128	1.530	52	1555	2585	1.6
2	0.7	0	133	1.673	66	2031	3263	1.66
3	1.05	0	132	1.795	58	1916	3060	1.59
4	0.5	5	122	1.897	65	1355	1538	1.13
5	0.7	5	128	1.930	69	1654	1986	1.2

has a negative effect on the yield of synthetic resin. Because of the impact of the indene on polymer structure, a rise in the softening point makes resins harder. Furthermore, these resins with high softening point look darker and can be used in the production of printing ink. Table 6 demonstrates the effect of toluene solvent on the characteristics of resins. In the presence of this solvent, the molecular weight and softening point decrease because in cationic polymerization, a series of transfer reactions can occur, and solvent transfer is one of these reactions. If a solvent has a high electronic density, solvent transfer takes place readily. This transfer reaction for solvents such as toluene and benzene is inevitable. Thus, due to solvent transfer reactions, chain growth stops and the acquired molecular weight for the synthesized resins becomes low. Eventually, there will be resins with a low softening point.

CONCLUSION

In this research work, we prepared petroleum resins from cationic polymerization of pyrolysis gasoline in the presence of $AlCl_3$ and BF_3 as catalysts. In so doing, a waste material is processed to become a highly valuable product. A survey of the factors involved in polymerization demonstrates that at low temperatures, 0-30°C are more suitable and appropriate for synthesizing resins with high molecular weigh and softening point and bright colours. When temperature goes up, increases the softening point and yield of resin are reduced. In the presence of BF_3 catalyst, resins with molecular weight above 1300-2000 (Dalton) and softening point of 100°C > were produced while with $AlCl_3$ catalyst, resins with the molecular weight ranging between 1000-1600 (Dalton) and the softening point less than 100°C were prepared. The optimal amount of catalyst to prepare resins with high softening point was 0.45-1.25 wt% of the feedstock. Another influential factor on the properties of the resins is the addition of indene and styrene as regulators of molecular weight and softening point. An increase in the amount of these materials in different percentages raises softening point significantly whereas reducing molecular weight and resin yield. When polymerizations takes place in the presence of aromatic solvents, the molecular weight and softening point reduce due to transfer reactions. Therefore, it is suggested to carry out the reaction with aliphatic solvents.

Tabriz, Iran for their valuable support and funding of this project.

ABBREVIATIONS

IC_4	Isobutane
NC_4	Normal butane
$1,4 C_5==$	1,4-Pentadiene
IC_5	Isopentane
NC_4	Normal pentane
$1C_5=$	Pentene
$2M1C_4=$	2-Methyl,1-butene
2M1,3BDN	2-Methyl,1,3-butadiene
$CYCC_5==$	Cyclopentadiene
$CYCC_5=$	Cyclopentene
$4M1C_5=$	4-Methylpentene
$CYCC_5$	Cyclopentane
$2MC_5$	2-Methylpentane
$3MC_5$	3-Methylpentane
NC_6	Normal hexane
$CIS-2C_6=$	Cis-2-hexane
$MCYCC_5$	Methylcyclopentane
BZ	Benzene
$3,3DMC_5$	3,3-Dimethylpentane
Tol	Toluene
NC_7	Normal heptane
NC_8	Normal octane
EB	Ethylbenzene
SM	Styrene
M,P XYL	m,p-Xylene
NPB	Naphthalene
DCPD	Dicyclopentadiene
Wt	Weight
Gc	Gas chromatography
Gr	Gram
CIS1,3DMCYCC5	cis-1,3-Dimethylcyclopentane
T-1,3DMCYCC5	trans-1,3-Dimethylcyclopentane
$T-1,2DMCYCC_5NC_7$	trans-1,3-Dimethylcyclopentane normal heptane

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