Union Production of Low Chlorinated Polyethylene and Chlorinated Paraffin via a Carbon Tetrachloride Solvent Free Process

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ABSTRACT: A novel process for producing low chlorinated polyethylene (LCPE) with chlorinity of 28–33% by weight is presented, in which a reactive solvent, paraffin, is used as a green solvent to replace the commonly used inert solvent, carbon tetrachloride (CTC), an ozone depleting substance (ODS) being phased out under the Montreal Protocol. This process utilizes the principle that paraffin can dissolve high density polyethylene (HDPE) at about 135°C and the resulting solution can be chlorinated by chlorine forming two useful products simultaneously, viz chlorinated paraffin (CP) and LCPE, which are mutual soluble even at lower temperature e.g.70°C. The present process is superior to the conventional CTC solvent method because it can reduce the solvent emission dramatically, enhance the volume efficiency of reactor and achieve a union production of LCPE and CP under atmospheric pressure. The structure and properties of LCPE produced by two different methods are determined by differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectrometer, proton magnetic resonance (^{1}H NMR), and gel permeation chromatography (GPC). The results indicate that polyethylene chain can be homogeneously chlorinated in paraffin as in CTC solvent via a radical mechanism, and the chlorinity of CP and LCPE is virtually same under optimal conditions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 63–69, 2009

Key words: chlorinated polyethylene; carbon tetrachloride; paraffin; reactive solvent; chlorination

INTRODUCTION

Low chlorinated polyethylene (LCPE) with chlorinity of ∼ 28–33% by weight and random chlorine substitution in polymer has been widely used for its unique properties,[1,2] because, on one hand, it has satisfactory resistance to most acids, bases, oil, and alcohols due to its saturated polymer backbone, and on the other hand, as an elastomer it shows extraordinary compatibility with a range of other materials.[3–5] By now, all LCPE used for the manufacture of printing ink and chlorosulfonated polyethylene (CSM) in China is produced via carbon tetrachloride (CTC) solvent method, where CTC is used as an excellent solvent for its good solubility for polymer and fully inertness to chlorine. For the same reason, many patents and articles have been reported on the preparation of LCPE by using CTC solvent.[6–11] However, such application of CTC as a solvent in chlorination reaction has to be phased out under the Montreal Protocol for eradicating ozone depleting substances (ODS) by 2010, so it is imperative to search an alternative solvent of CTC. For this purpose, much research has been carried out and some solvents have been investigated.[12–14] These solvents can be divided into four categories in general, viz (1) chlorinated methanes, e.g. chloroform and methylenedichloride, (2) chloro-substituted ethane or ethylene, e.g. trichloroethylene, tetrachloroethane, and ethylene tetrachloride, (3) chloro-substituted benzene, e.g. chlorobenzene, monochloromonofluorobenzene, and mixtures thereof, and (4) water. It can be seen that all these attempts are directed to screen a solvent which is fully or at least partially inert to chlorine so as to mimic the attributes of CTC. However, further chlorination is inevitable for the first three kinds of solvents, forming byproduct of CTC, hexachloroethane, and polychlorinated benzene, respectively. This is not acceptable in view of the reduction of ODS or unwanted toxic residues in LCPE product. On the contrary, water is totally inert to chlorine, however, it fails to provide a homogeneous chlorination condition for suspended high density polyethylene (HDPE) particles and thus less appropriate as a solvent for the production of low chlorinity LCPE with uniform chlorination.[15]

Now that it is too difficult to find a suitable solvent being comparable with CTC in terms of inertness to chlorine, cost-effectiveness and ease of separation, why do not we try a solvent which can be chlorinated simultaneously with HDPE forming two useful chlorinated products, i.e., LCPE and chlorinated solvent, in one pot. Toward this end, no report has been available till now to our best knowledge. In such way, the reactor can be used much more efficiently than the conventional production process of LCPE, since in the CTC solvent process, the mass fraction of LCPE is only about 10% and the remaining 90% is CTC solvent. In this report, paraffin is chosen as a reactive solvent because it can dissolve HDPE at higher temperature, and its chlorinated form, chlorinated paraffin (CP), can dissolve LCPE. Therefore, the whole reactions always take place in homogeneous solution, which is helpful for LCPE product with uniform chlorination. Considering that CP with chlorinity of 10–65% is a volume chemical widely used in plastic industry,[16,17] and that paraffin is sparsely volatile and much less toxic than traditional volatile organic solvents like CTC, the present union production process is more efficient and environmental friendly.

EXPERIMENTAL

Materials and apparatus

All solvents and reagents were purchased from commercial sources in China and used as received. HDPE (melting temperature 130°C) was kindly supplied by Jilin Chem. Corp. Ltd. of Sinopec. Chemical grade of paraffin (an acyclic mixture with boiling point above 300°C and carbon atoms ranging from 12 to 15), and AR grade of AIBN and acetone were obtained from Tianjin Damao Chem Reagent Factory. Chlorine gas of industrial grade was purchased from Beijing Second Chemical Factory.

The reaction was carried out at atmospheric pressure in a four-hatch flask immersed in thermostatic oil bath. The reactant mixture was stirred vigorously using a mechanical mixer, the reaction temperature was monitored with glass thermometer, the flow rate of chlorine gas into the reactor was detected by a gasometer. The effluent gas containing superfluous chlorine and hydrochloric (HCl) gas was scrubbed by sodium hydroxide (NaOH) dilute solution.

Preparation of LCPE and CP

To a 250-mL flask, 5 g granular HDPE and 100 mL paraffin were added. After 1 h stirring for the mixture at 135°C, HDPE particle dissolved completely into paraffin forming a homogeneous and transparent liquid. Then 0.5 g AIBN was added to the flask

and chlorine gas was introduced at flow rate of 6.0–6.5 g/h for 5 h uninterruptedly. Later, the reaction temperature was lowered gradually to 70°C and chlorine gas was continuously fed into the reactor at the said flow rate for 10 h until the chlorinity of LCPE reached 28–33%, by weight. When the chlorination finished, nitrogen gas was introduced to strip the residual chlorine and HCl gas in the reactor. Then the reaction mixture was cooled down to room temperature, to which twofolds volume of acetone was added forming LCPE solid precipitate and CP solution of acetone. The LCPE precipitate was washed twice with small amount of acetone and once with deionized water and then dried overnight in an oven at 80°C. CP and acetone was separated via simple distillation followed by rotary vacuum vaporization to remove all volatile components.

Property measurement of LCPE and CP

The chlorinity of LCPE and CP is determined quantitatively by sample combustion and chemical titration of chloride anion.[18] For this measurement, 20–30 mg of LCPE or CP was weighted accurately with balance, wrapped with a filter paper and then inserted immediately into a combustion flask after ignition, in which 25 mL 1.0 mol/L NaOH solution and pure oxygen was filled beforehand. After combustion, the flask was sealed for at least 30 min to ensure that all HCl gas produced was completely absorbed in NaOH solution. And then the chloride concentration was analyzed according to the standard procedure using silver nitrate as titration solution and potassium chromate as indicator.

Viscosity of CP liquid at different temperatures was measured using rotary viscometer (NDJ-1, Shanghai Scale and Instrument Co., Ltd) according to the operation instruction.

The chroma of LCPE was measured in terms of the absorbency of its 20% solution of toluene using Ultraviolet-Visible spectrophotometer (752 model, Shanghai Precision and Scientific Instrument Co. Ltd.) at wavelength of 450 nm according to the procedure outlined in the enterprise quality standard of LCPE.

DSC

Calorimetric measurements were performed in a differential scanning calorimeter (NETZSCH DSC 204 F1, Germany) at a heating rate of 10°C/min under nitrogen atmosphere and the temperature ranged from 40 to 160°C. The crystallinity for samples (HDPE, LCPE1, and LCPE2) was calculated by using the following expression:
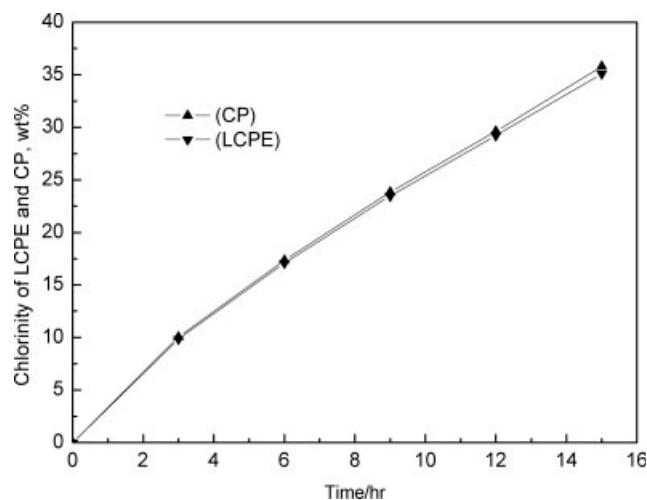
Figure 1 The chlorinity of LCPE and CP at different reaction period; The reaction condition is same as that noted as a in Table I.

$$\text{Crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^0} \times 100\%$$

where ΔH_f^0 is the heat of fusion of 100% crystalline of HDPE and ΔH_f^* is the heat of fusion of samples.

IR spectroscopy

IR spectra of the polymers HDPE and LCPE were recorded using a Fourier transform infrared (FTIR) spectrometer (Nexus 8700, USA) with attenuated total reflection instruments. The polymers were taken on the flat sheet and data were collected over 32 scans with a resolution of 8 cm^{-1} at room temperature.

^{1}H NMR spectroscopy

High-resolution proton magnetic resonance (^{1}H NMR) spectra were recorded using a 600 MHz Bruker av600 spectrometer (Switzerland), in CDCl$_3$ at room temperature and tetramethylsilane (TMS) as an internal reference.

GPC

Gel permeation chromatography (GPC, Polymer Laboratories GPC220, England), with a polystyrene column in the GPC-viscometer module, was used for characterization of molecular weights and weight distributions of the polymer fractions at 150°C. Molecular weight was calculated with a standard procedure based on the universal calibration curve of polystyrene.

RESULTS AND DISCUSSION

Chlorination synchronicity of LCPE and CP

The formula of LCPE and CP with chlorinity of ~ 30% by weight can be roughly represented by [C$_{12}$H$_{24}$Cl$_2$]$_n$ and C$_{12}$H$_{24}$Cl$_2$, respectively. As shown in Figure 1, the chlorinity of both LCPE and CP increased steadily with time in an approximately identical rate. This may be ascribed to the close similarity in structure between paraffin and HDPE, i.e., both dominated by methylene group, as well as good solvency of paraffin to HDPE that make the polymer chain well stretched in the solution, having the chlorination rate of polymer as same as that of paraffin.

The results show that LCPE and CP with chlorinity of about 30% can be produced simultaneously, which justified the present process in technical point of view. It is well known that higher temperature makes for the reduction of liquid viscosity and increase of chlorination rate, but can result in a higher energy cost and thermal decomposition of the chlorinated products. To investigate the influence of reaction temperature on the chlorination synchronicity, some experiments are carried out and the chlorinity of CP and LCPE at different time is measured, as listed in Table I. As seen from Table I, the chlorinity difference between CP and LCPE is negligible for all reaction conditions except e, which suggests that at least 3 h high temperature chlorination is necessary for destroying the crystal structure of polymer and then the chlorination reaction can precede synchronicity at lower temperature, e.g., 70°C. Among

TABLE I
Instant Chlorinity of CP and LCPE at Different Reaction Condition (%, by weight)

Chlorination condition	a		b		c		d		e	
Sampling time/h	CP	LCPE	CP	LCPE	CP	LCPE	CP	LCPE	CP	LCPE
3	10.05	9.86	9.19	8.85	10.16	9.54	9.47	9.60	9.45	3.67
6	17.33	17.09	16.71	16.46	17.31	16.01	16.54	16.49	18.49	6.72
9	23.83	23.46	22.71	22.32	24.09	23.18	24.79	24.45	24.28	9.14
12	29.63	29.23	29.43	28.62	31.65	30.87	31.02	30.31	30.72	10.29
15	35.81	35.10	35.07	35.04	36.08	34.94	36.22	35.74	35.74	10.64

Note: In the reaction process, the chlorination temperature and duration are as follows: a) 135°C (15 h); b) 135°C (3 h) + 70°C (12 h); c) 135°C (1 h) + 105°C (2 h) + 70°C (12 h); d) 105°C (3 h) + 70°C (12 h); e) 105°C (1 h) + 70°C (14 h).

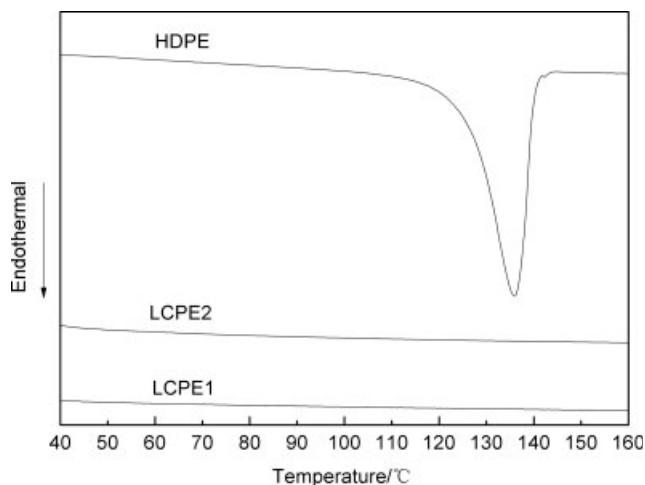**Figure 2** DSC curves for HDPE, LCPE1 and LCPE2; heating rate 10°C min^{-1}.

the chlorination conditions *a* through *d*, *d* is recommendable considering its longer chlorination time at lower temperature.

Crystallizability of LCPE

HDPE is a crystalline polymer. To make it soluble in organic solvent at room temperature, the crystalline structure has to be destroyed completely, and the grafting of the polymer chain, for example via chlorination, is a commonly used method. The crystallizability of LCPE products, viz LCPE1 prepared using paraffin and LCPE2 prepared using CTC, is determined through DSC analysis and compared with HDPE raw material. As shown in Figure 2, the crystallizing temperature of HDPE is around 135°C, and the apparent crystalline degree is 65.8% as estimated by the fusion heat of DSC measurement.[19,20] However, no endothermic peak is found for LCPE1 and LCPE2 sample, suggesting that the LCPEs thus produced with chlorinity of about 30% is of noncrystallinity. This may be attributed to the steric hinderance of the randomly distributed chlorine atoms grafted into the polymer chains, which prohibited the crystallization of the polymer strip. The crystalline temperature of HDPE also suggested a reasonable temperature range for homogeneous dissolution and chlorination of the polymer blend.

Homogeneity of chlorine distribution in LCPE

The microstructure of HDPE, LCPE1 and LCPE2 is studied by infrared spectra, as shown in Figure 3. It is seen that the IR spectra of LCPE1 and LCPE2 are virtually same, while the difference of IR spectrum between LCPEs and HDPE is noticeable. In the IR spectrum, the absorption frequencies in 2750–3000 cm^{-1} can be assigned to C—H stretching vibration of

methylene group —CH$_2$—. It is noted that the characteristic absorption of LCPE is wider and more important than that of HDPE, i.e., the wave number of methylene group is shifted from (2848.0 and 2915.0 cm^{-1}) in HDPE to ($\sim$ 2855 and $\sim$ 2930 cm^{-1}) in LCPE due to the presence of C—Cl bond.

The absorption of HDPE at 718.4 cm^{-1} can be assigned to methylene rocking mode in polyethylene crystallites[21] due to the presence of (CH$_2$)$_x$ ($x \geq 4$) segments in the polymer. However, in the chlorinated polymers, i.e., LCPE1 and LCPE2, the characteristic absorption at this frequency disappeared. This indicates that the crystalline structure is destroyed completely, being consistent with the DSC observation. Besides, the chlorine is evenly distributed in the polymer chain as a result of thorough dissolution and nonfolding structure of polymer otherwise residual crystallite will be detected. Therefore, the present method can be deemed as a homogeneous solution chlorination process similar to the conventional CTC solvent method.

The absorption at 1468 cm^{-1} for HDPE can be assigned to bending vibration of the methylene group in the polymer, and this absorption is shifted to 1457.0 cm^{-1} for LCPE1 and 1458.5 cm^{-1} for LCPE2, respectively, due to the influence of chlorine substitution. The —CH deformation mode appeared at 1260 cm^{-1} in the spectra of LCPE1 and LCPE2 proved the presence of the structure of —CH$_2$—CHCl— in the chlorinated polymer.

To examine the fine structure of the chain segment with respect to LCPE, the fingerprint region of HDPE, LCPE1, and LCPE2 in the frequency range of (500–1000) cm^{-1} is portrayed in Figure 4. It is noted that in comparison with the spectrum of HDPE, five new peaks, namely, 609, 659, 733 $\pm$ 1, 789 $\pm$ 5, and 913 cm^{-1}, were recorded for LCPE1 and LCPE2 in the range of 600–1000 cm^{-1}, which is probably
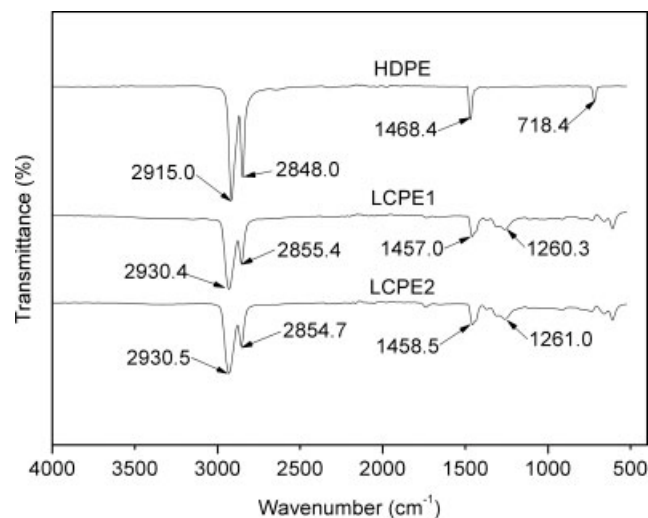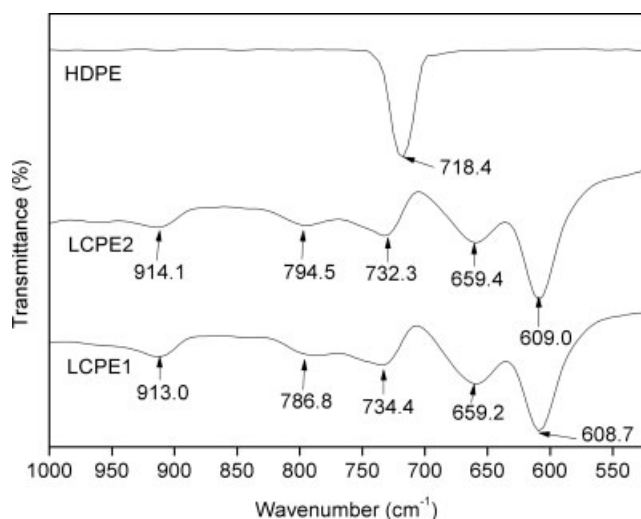

Figure 3 Infrared spectra of HDPE, LCPE1, and LCPE2.

Figure 4 Infrared spectra of HDPE, LCPE1, and LCPE2; Wavenumber from 500 to 1000 cm^{-1}.

Figure 6 GPC curves of HDPE, LCPE1, and LCPE2.

related to the stretching vibration mode of C—Cl bond in the chlorinated polymer. For example, the wave number appearing at about 732 and 789 ± 5 cm^{-1} can be assigned to C—Cl of the structure —CH$_2$—CH$_2$—CHCl— at the chain end.[22] It is also noted that there is not any band in the region below 600 cm^{-1} in the spectra of LCPE1 and LCPE2. This observation suggests that polyethylene is chlorinated in the form of —CHCl— and that hardly any —CCl$_2$ units are formed, otherwise, a strong band assigned to the —CCl$_2$ stretching mode should appear at 527 cm^{-1}.[23] The negligible difference of LCPE1 and LCPE2 in IR spectra may be ascribed to the similar chlorination conditions provided by paraffin and CTC solvent, i.e., they are both of chlorination reaction in a homogeneous solution following radical substitution mechanism.
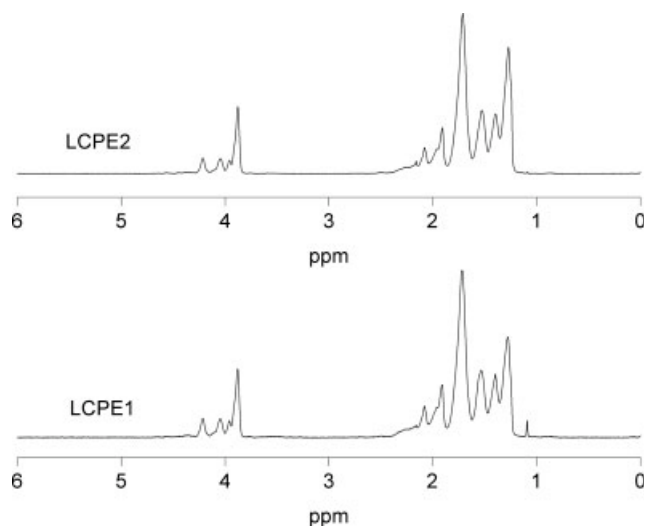
Chlorinity of LCPE from ^{1}H NMR

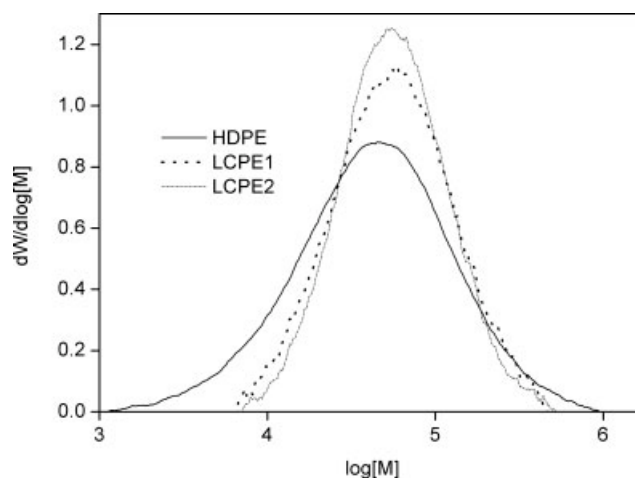The ^{1}H NMR spectra of LCPE1 and LCPE2 were recorded and presented in Figure 5. As shown in Figure 5, the chemical shift can be divided into two bands, i.e., from 1.2 to 2.2 ppm and from 3.8 to 4.2 ppm, corresponding to the proton resonances in —CHCl— and —CH$_2$— group, respectively, since the first band is absent in polyethylene and thus is unique for LCPE.[24,25] On this basis, the chlorinity of LCPE1 and LCPE2 can be estimated from the corresponding ^{1}H NMR spectroscopy in terms of the integrated peak areas of the two bands. For example, the ^{1}H NMR integral area for —CHCl and —CH$_2$— group is 2.822 and 19.927, respectively, for LCPE1, and thus the chlorine content is calculated as 36.25% by the following equation:

$$Cl\% = \frac{2.822 \times 35.5}{2.822 \times M_{CHCl} + (19.927/2) \times M_{CH_2}} = 36.25\%,$$

where M_{CHCl} and M_{CH_2} are molar mass of group —CHCl— and —CH$_2$—, respectively. Considering the H-atom in —CH$_2$— is twice of that in —CHCl— group, the peak area of —CH$_2$— is divided by 2 for normalization. And similarly, the chlorine content of LCPE2 is calculated as 35.57%, which is virtually consistent with the experimental value of 33.12% determined by chemical titration method.[18]

Figure 5 ^{1}H NMR spectra of LCPE1 and LCPE2.

TABLE II
Characteristic Data of HDPE, LCPE1, and LCPE2 by GPC

Polymer	M_n (g/mol)	M_w (g/mol)	Polydispersivity
HDPE	23,800	72,592	3.11
LCPE1	40,926	76,801	1.88
LCPE2	44,039	74,417	1.69

TABLE III
Technical Comparison for Conventional Method and the Present Method

Details	Conventional method	Present method
Reaction temperature	From 110 to 78°C	From 135 to 70°C
Reaction pressure(absolute)	0.3 MPa	0.1 MPa
Emission of ODS, kg/t- LCPE	350–500 kg CTC	0
Emission of solvent, kg/t- LCPE	350–500 kg CTC	<30 kg acetone
Use efficiency of reactor	10%	100%
Output	LCPE	LCPE and CP
Usability of chlorine	Near to 100°C	Near to 100°C
Chlorinity of LCPE	20–40%	20–40%
Product separation	Distillation/vacuum drying	Solvent precipitation/distillation
Reaction time	Short	Long

Variation of molecular weight distribution of LCPE

GPC curves were recorded for polymer HDPE, LCPE1 and LCPE2, as presented in Figure 6, and the key indices are summarized in Table II with respect to number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersivity. As seen from Figure 6, the shape of molecular weight distribution of LCPE1 and LCPE2 is similar, indicating the similarity of chlorination process in two different solvents, viz paraffin and CTC. Compared with HDPE, the molecular weight distribution of LCPE (including LCPE1 and LCPE2) becomes higher and narrower, which is in line with the lowering polydispersivity of LCPE1 and LCPE2, as shown in Table II. The lowering polydispersivity of LCPE in comparison with HDPE may be ascribed to the following facts. On one hand, some LCPE with low molecular weight may be dissolved in acetone like CP. On the other hand, some HDPE with high molecular weight may degrade at higher temperature for a long period of time, which may lower the M_n of the polymer. Besides, some side reactions may take place between paraffin or CP with HDPE or LCPE1 via a radical mechanism. Because of the chain scission or thermal degradation of polymer, the measured M_n of LCPE1, 40,926 g/mol, is lower than the theory value of 44,900 g/mol. The lower M_n of LCPE1 with respect to LCPE2 further justified the thermal chain scission assumption.

Technical comparison for CTC and paraffin solvent methods

To show the feasibility of the present process for the production of LCPE, the main operation conditions and characteristics are outlined in Table III. It is seen that although the initial reaction temperature in the present process is somewhat higher for the sake of complete dissolution of HDPE, the pressure is reduced dramatically due to the negligible volatility of paraffin. This is helpful for reducing the risk of toxic gas leakage and increasing the safety of industrial operation. And more importantly, CTC solvent can be replaced by a greener one, paraffin, for phasing out such application of CTC, since CTC is an ODS being banned by the Montreal Protocol for the protection of ozone layer. In addition, some other advantages of the present process also deserve mention. First, the emission of VOC is reduced greatly from 350–500 kg CTC to an estimated 30 kg acetone per ton of LCPE product due to the difference in emission ways. The majority of CTC solvent is emitted via offgas of the chlorinating and purging process at high temperature, while acetone is emitted only in the separation process of LCPE at low

TABLE IV
Property Comparison of LCPE Produced by Different Method

Quality indices	Conventional method	Present method
Chlorinity	31.65%	33.61%
Dissolubility in toluene	Complete dissolution	Complete dissolution
Homogeneity of LCPE[a]	Transparent	Transparent
Absorbency[b]	1.338	1.189
PH value in water[c]	6.32	5.89

[a] Homogeneity of 20% LCPE solution of toluene is measured via eye measurement.
[b] The absorbency of 20% LCPE solution of toluene is measured with 752-photometer at wave length of 450 nm.
[c] To 35 g 20% toluene solution 28 g deionized water was added, stirred 30 min and settled 60 min, and then the PH value of the water layer is determined using PH-meter.

TABLE V
Viscosities of CP made by different methods at varying temperature

Temperature (°C)		20	30	40	50	60
Viscosity (Pa s)	Conventional method	73.3	24.7	7.6	3.1	1.4
	Present method	75.4	27.2	8.2	3.4	1.5

temperature. Second, the use efficiency of reactor is enhanced from 10 to 100%, because in the conventional process 90% of the reactor is taken up by CTC solvent, while in the present process 90% is taken up by a paraffin solvent that will be converted concurrently to another useful product CP. Therefore, the present process is a more efficient and energy-saving process. Finally, the usability of chlorine as well as the quality of LCPE is virtually same.

Properties of LCPE produced by CTC and paraffin solvent method

To compare the product quality of LCPE produced by CTC solvent and paraffin solvent method, some properties of LCPE are measured, e.g., chlorinity, dissolubility in toluene, absorbency (20% LCPE solution of toluene, by weight) etc, and presented in Table IV. It should be pointed out that the contrast LCPE product was supplied by Jilin Chemical Corp. Ltd of Sinopec using CTC solvent process technology. The results indicate that the quality difference of LCPE produced by the two methods is negligible. Therefore, paraffin can be used as a promising reactive solvent to replace CTC, an inert solvent to chlorine, for the production of LCPE.

Properties of CP produced simultaneously with LCPE

It is known that chlorinated paraffin (CP) with chlorinity of 10–50% is commercially produced by directly chlorinating liquid wax with chlorine at elevated temperature in the presence of radical initiator AIBN. This process is nearly identical to the present process for the production of LCPE except the coexistence of some HDPE or its chlorinated form. Table V shows the viscosity of CP samples at different temperature measured with a rotary viscometer. It is shown that the viscous behavior of these two CP samples is of great similarity, however, the viscosity of CP coproduced is somewhat higher than that made by conventional method, which is likely due to the residue of the chlorinated low molecular HDPE in CP product.

As an extension of the present approach, LCPE may be either produced as a byproduct by the present manufacturers of CP, or paraffin may be replaced with other reactive solvents provided that

their chlorinated form is of value and great demand in industry.

CONCLUSIONS

A novel process is proposed which utilizes paraffin as a reactive solvent to replace CTC, an ODS, in the manufacture of LCPE, leading to a coproduction of LCPE and CP. Microstructure and properties of the product is analyzed by DSC, FTIR, ^{1}H NMR, and GPC. It is shown that the product quality of LCPE and CP coproduced with the present process is comparable with the conventional one. Further, the present process is superior to the conventional one in terms of VOC emission, use efficiency of reactor, operation condition, and more importantly phaseout of ODS in manufacturing chlorinated polymer.

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