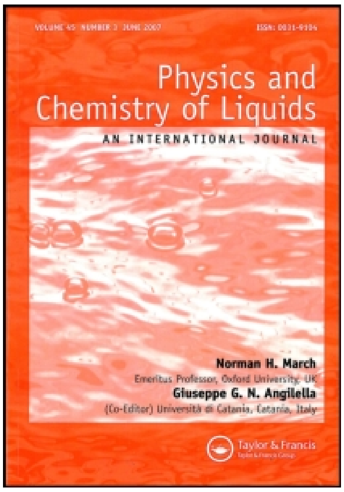

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Determination of three-dimensional solubility parameters of chlorinated polypropylene by ultrasonic degradation

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The degradation reactions of chlorinated polypropylene (CPP) in toluene under ultrasonic irradiation were studied. The Mark–Houwink equation acquired from fractional precipitations was also suitable for estimating the molecular weight of degraded CPP. An objective standard was proposed for judging the solution behaviour of CPP in solvents by the study on the relative solubility of CPP before and after degradation. Then Hansen three-dimensional solubility parameters and the total parameter of CPP were obtained by optimization calculation in terms of the criterion proposed here. It was proved that the total parameter of CPP is creditable by the turbidity method. Compared to other standards, the result obtained from the proposed standard accorded well with the standard of complete miscibility suggested by Flory–Huggins for polymers and solvents as well as the objective reality. This standard may provide a reference for other polymers.

Keywords: Chlorinated polypropylene; Ultrasonic degradation; Solubility parameter; Dilution ratio

1. Introduction

Chlorinated polypropylene (CPP) has excellent abrasion resistance, age resistance as well as acid and alkali resistance. It also has an excellent adhesion to polyolefin. As an adhesion promoter, CPP is widely used in polyolefin coatings, agglutinants, printing ink and in compatibility assistants, etc [1].

The CPP is normally used in solvents, so it is an important fundamental work to investigate its solubility parameter to predict the solution behaviour in various solvents. However, to the best of our knowledge, there is no systematic report on the investigation of the solubility parameter for CPP. In this article, the solubility parameter of CPP is studied systematically.

The concept of a solubility parameter was first presented by Hildebrand. He considered that in a system where the dispersion forces were predominant, the solvent could dissolve the polymer when their parameters were close. However, the molecule

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polar as well as the hydrogen bonding interaction between the polymer and the solvent must be considered in the solutions of polar polymer–solvent system. In order to predict the miscibility of various polymer–solvent systems, various modifications have been made for the method of solubility parameter. It is the method of Hansen three-dimensional solubility parameters that are recognized widely at present. Hansen divided the total solubility parameter δ into three values – δ_d, δ_p and δ_h – where δ_d, δ_p and δ_h are the contributions of dispersion forces, dipolar forces and hydrogen bonding, respectively. Only when the three-dimensional solubility parameters of the polymer and the solvent are all close, can the solvent dissolve the polymer. The objective of this work is to determine the three-dimensional solubility parameters for CPP precisely.

Total solubility parameters of solvents can be obtained from the definition $\delta = (\Delta E / V_m)^{1/2}$ by the energy of vaporization ΔE and the molar volume V_m. Since polymers cannot vaporize normally, total solubility parameters of polymers cannot be acquired by the definition. Their values of three-dimensional and total solubility parameters should be acquired by experiments.

The experimental method to determine the three-dimensional solubility parameters of a polymer is as follows. First, a polymer is dissolved in various solvents under a certain concentration; second, the solvents are divided into good and bad solvents and the solubility parameters of the polymer are calculated using the solubility parameters of the good solvents. Because the molecule size of polymers and solvents are quite different, the solution behaviour of polymers is always a complex process. Besides the thermodynamics solution equilibrium, dynamic resistance of the solution process should also be taken into account. Consequently, for the sake of minimizing the solution time, researchers often reduce the concentrations of polymers to determine the good and poor solvents. For example, the concentration of polymers selected by Lieberman [2] is 3% by weight; Hansen's method [3] is that 0.5 g polymer is put into 5 mL solvent; Funasaka's method [4] is that 0.02 g of polymer sample is fed into 0.98 g of solvent; and Wiehe [5] selected $4\,\mathrm{g\,L^{-1}}$ as the concentration of polymers. The experiments were generally carried out at room temperature. The solution results were observed by visual inspection.

Thermodynamics of polymer solution [6] indicates that whether a polymer dissolves in a solvent spontaneously is decided by the free energy of mixing. The expression of free energy of mixing is:

$$\Delta F_m = \Delta H_m - T\Delta S_m \tag{1}$$

where ΔF_m, ΔH_m and ΔS_m are the free energy, enthalpy and entropy of mixing, respectively. Only if the free energy of mixing is less than zero, can the solvent dissolve a polymer spontaneously. By means of the lattice theory, Flory–Huggins applied the statistical thermodynamics to deduce the following equations:

$$\Delta F_m = RT(n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + \chi_{12} n_1 \varphi_2) \tag{2}$$

where R is the gas constant and T is the Kelvin absolute temperature; n_1, φ_1, n_2, φ_2 are the molar fraction and the volume fraction of the solvent and the polymer, respectively and is the Flory–Huggins interaction parameter.

$$\Delta \mu_1 = \left[\frac{\partial(\Delta F_m)}{\partial n_1}\right] = RT\left[\ln \varphi_1 + \left(1 - \frac{1}{x}\right)\varphi_2 + \chi_{12}\varphi_2^2\right] \tag{3}$$

where $\Delta\mu_1$ and x are the chemical potential change of the solvent and the degree of polymerization of a polymer respectively. As shown in equation (3), whether a polymer dissolves in a solvent is directly related to χ_{12}, φ_2 and x. In fact, φ_2 can be regarded as the concentration of a polymer.

χ_{12} is the intrinsic parameter of a polymer and a solvent. For a definite polymer–solvent system, the value of χ_{12} is certain in theory. Therefore, the chemical potential change of the solvent is decided by the concentration and the degree of polymerization of the polymer. To determine the solubility parameter of a polymer, one needs to investigate the solution behaviour in various solvents, so that various values of interaction parameters and concentrations of polymer may appear certainly. The value of $\Delta\mu_1$ may be bigger, less than zero or equal to zero. Accordingly, it is unavoidable that no solution and partial solution may happen. For instance, a polymer can dissolve in a solvent at 0.4%, but it is uncertain whether the polymer can dissolve in the solvent at 3%, 10% or more than that. We consider that the standards described above to judge good and poor solvents are subjectively stipulated by the experience of different researchers. The suggestion in this article is to find an objective standard for judging good and poor solvents and to calculate the three-dimensional solubility parameters of CPP by this standard precisely.

The solubility of a polymer in a solvent is concerned with the molecular weight (degree of polymerization). For a polymer with low molecular weight, the solubility is better than that for a polymer with high molecular weight. This is one important basis for fractionated precipitation [7]. The method used in this work is to investigate the solubility from the degree of polymerization of polymers and is applied to determine the three-dimensional solubility parameters of CPP. In [8], Da-Zhuang Liu *et al.* had separated CPP using fractional precipitations by solvent/nonsolvent technique and obtained a series of samples whose weight-average molecular weights (M_w) were 91,500–326,900 g mol^{-1}. But the differences of molecular weights were still too small to see the distinction of solubility evidently. Consequently, the method of ultrasonic degradation is applied to acquire the samples with lower molecular weights to investigate the effect of molecular weight on the solution behaviour.

2. Experimental

2.1. *Materials*

CPP, which contains 30% chlorine by weight, is a commercial product purchased from Jin Zhujiang Chemical Factory in Guangdong (China). The viscosity-average molecular weight of CPP is 174,592 g mol^{-1}. Toluene is of A.R. grade.

2.2. *Experiments of ultrasonic degradation*

The reactor is a 450 mL glass vessel with a jacket to keep the temperature constant at 20°C during the sonication. Ultrasonic irradiation is carried out using a JY92-II cell disintegrator, made by NingBo (China) XinZhi Biochemical Controlled Limited Company, operating at 68% of its full intensity, which is 650 W nominally at 20–25 kHz. The ultrasonic probe with a flat surface of 6 mm in diameter contacts directly the sample solution. The volume of the sample solution is 240 mL.

The concentrations of CPP in toluene solution are 1, 10 and 20%. At certain intervals, samples are removed. The samples are dried by vacuum until the weights are invariable.

2.3. *Molecular weight measurement*

A DAWNEOS multi-angle laser photometer from Wyatt Technology Corp. was used as the mass and size detector. An LC-10AVP chromatogram instrument (from Shimadzu Corporation) completed the equipment. Tetrahydrofuran (THF) freshly distilled from sodium and benzophenone, filtered through a membrane (0.22 μm) and degassed, was used as eluent at a flow rate of $0.5\,\mathrm{mL\,min^{-1}}$. Dried CPP is put into THF solution. The concentration is $10\,\mathrm{mg\,mL^{-1}}$. The volume of the sample required for measurement is 100 μL.

2.4. *Measurement of intrinsic viscosity*

The intrinsic viscosity ($[\eta]$) of degraded CCP is measured by Obblehode Viscometry. The values of $[\eta]$ are calculated according to [9].

2.5. *Measurement of relative solubility*

The undegraded and degraded CPP is put into a special solvent at 298.15 K for three days. The sample is shaken for a certain time and the solution is filtrated, and the polymer content in the clear solution is determined by weighing method. The polymer solubility is obtained by calculating dissolving polymer quantity for every 10 mL of solvent. The solubility of degraded CPP is determined using the 1% sample degraded for 900 min under ultrasonic irradiation. Since the solution time is only three days, the value of solubility obtained should be the relative solubility. This article continues the method described in [8].

2.6. *Turbidity method and solubility parameter*

It is well known that toluene is a good solvent while hexane and methanol are nonsolvents for CPP. Hexane or methanol is dripped into the toluene solution to turbidity. The CPP toluene solution taken is exactly 5 mL and its concentration is $13.9\,\mathrm{mg\,mL^{-1}}$. The volumes of hexane or methanol are recorded when turbidity happens. The volume fraction ϕ_i (toluene volume or nonsolvent volume/sum volume after titration) is calculated. The solubility parameter δ_{sm} of mixed solution could be calculated by means of the following formula, $\delta_{\mathrm{sm}} = \phi_1\delta_1 + \phi_2\delta_2$, where ϕ_1, δ_1, ϕ_2 and δ_2 are the volume fraction and solubility parameter of toluene and nonsolvent, respectively. According to [10], the solubility parameter of mixed solvent of toluene and hexane is the lower limit of the sample (δ_{low}). The solubility parameter of mixed solvent of toluene and methanol is the upper limit of the sample (δ_{high}). The mean value of the lower limit and the upper limit is the point estimation value of the sample ($\delta_{\mathrm{average}}$). The 1% sample is used to determine the point estimation value of solubility parameter for degraded CPP.

Table 1. The molecular weights and intrinsic viscosities of degraded CPP at various concentrations.

No.	Sample	Time (min)	M_w	M_n	M_w/M_n	$[\eta]$ (mL g^{-1})
1	20% CPP	1200	93,140	85,400	1.091	51.323
2	10% CPP	1320	66,190	60,940	1.086	40.944
3	1% CPP	900	43,420	30,450	1.426	28.754

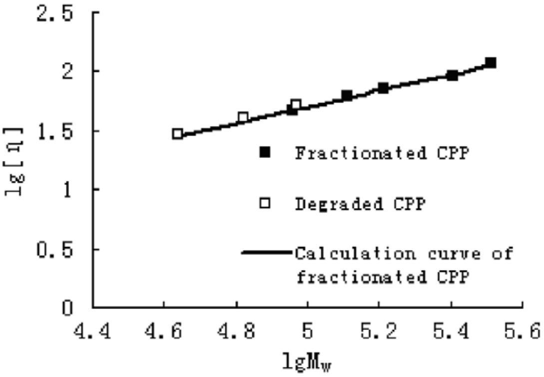

Figure 1. The relation of weight average molecular weight (M_w) and $[\eta]$ of fractionated as well as degraded CPP.

3. Results and discussion

3.1. *The characters of degraded CPP*

Compared with undegraded CPP, no new absorption peak appears on the FTIR spectra of degraded CPP. This indicates that the molecule structure of degraded CPP does not change. After analysis for each degraded sample, it is found that the chlorine content is also 30%, i.e., the same as that of undegraded CPP. So the Mark–Houwink equation proposed in [8] can be applied to the degraded CPP, in principle. But the application condition of the equation is related to the configuration – how the molecules of CPP exist in solution. Only if the configuration of molecules of CPP is similar, the equation can be used. Accordingly, whether degraded CPP and fractionated CPP all obey the same Mark–Houwink equation is the first step of this study.

The molecular weights and $[\eta]$ of degraded CPP are listed in table 1. From the results listed in table 1, the molecular weights of degraded CPP apparently decrease.

The original data of the Mark–Houwink equation $[\eta] = 0.0174\,M^{0.6919}$ for fractionated CPP in [8] are plotted in figure 1. The molecular weights and $[\eta]$ of degraded CPP listed in table 1 are also plotted in figure 1, the experimental points are located on the line of the Mark–Houwink equation. So, degraded CPP, and fractionated CPP, all obey the same Mark–Houwink equation. This indicates that the molecules of degraded CPP in toluene also exist as random coil. That the structure of molecules, chlorine content, and the configuration of molecules in toluene solution do not change indicates that other characters except the molecular weight are the same as undegraded CPP. Therefore, a foundation is established for further investigation of the effect of molecular weight on dissolvability.

Based on this, the relative solubility of the degraded sample (1%) with the lowest molecular weight is determined in various solvents and is compared with that of undegraded CPP.

3.2. *The relative solubility of CPP with various molecular weights*

The values of the relative solubility of CPP before and after ultrasonic degradation in 28 solvents are listed in table 2. It is found that the number of increscent solubility is 15 after decrease of molecular weight and the number of invariable solubility is 13. The solubility that does not change with molecular weight is small, while the solubility that changes with molecular weight is relatively large. The least solubility is in Butanone (No.15) among the 15 increscent values of solubility. The highest solubility is in Methylpyrrolidone (No.16) among the 13 invariable values of solubility. On further investigation, it is found that if the variable values of solubility are plotted, the values of solubility of degraded CPP are linear with the values of solubility of undegraded CPP and the data fit of 0.98 is very good.

This phenomenon is attributed to the following reasons: Whether a polymer can dissolve in a solvent or not is decided by the structure unit of the polymer and the composition of the solvent. When ΔF_m is bigger than zero in the whole or most range of φ_2, the polymer does not dissolve in the solvent and the solubility cannot increase by means of decreasing the molecular weight of the polymer. Only the condition that ΔF_m is less than zero is satisfied in the whole or most range of φ_2, may the solubility increase by means of decreasing the molecular weight of the polymer. Data in figure 2 agree well with the latter. Based on such reasons, an assumption is presented that whether the solubility increases or not after ultrasonic degradation, is regarded as the boundary for judging the solution and no solution. Solvents can be classified into two kinds in terms of this boundary. One is as a good solvent if the relative solubility in it increases with the decrease of molecular weight; the other is as a poor solvent if the relative solubility in it does not change with the molecular weight. According to this assumption, the solubility in Butanone – $0.39\,\text{g}/10\,\text{mL}^{-1}$ of solvent – is on the solubility boundary for CPP.

It is necessary to note that the solubility parameter is not concerned with the molecular weight normally. We also insist on this viewpoint in this article. What we investigate in this work according to the proposed classification method for solution behaviour is to propose a standard for judging good and bad solvents of CPP and to calculate the three-dimensional solubility parameters of CPP by this standard precisely, but not to investigate the solubility parameter change of CPP before and after ultrasonic degradation. Of course, the feasibility of the standard is determined by whether the calculated solubility parameter of CPP is reasonable (see next subsection).

3.3. *Three-dimensional solubility parameters of CPP*

The basic method of Hansen solubility parameters is that the total solubility parameter is a vector composed of components representing hydrogen bonding, polar, and

Table 2. The relative solubility of CPP, solubility parameters of solvent and interaction radius as well as χ_{12}.

		Relative solubility (g/10 mL^{-1})		Solubility parameter (J cm^{-3})$^{1/2}$				Interaction radius (J cm^{-3})$^{1/2}$		
No.	Solvent	Undegraded	Degraded	δ [11]	δ_d [12]	δ_p [12]	δ_h [12]	This article	Hansen	χ_{12}
1	Xylene	3.57	4.99	18.00	17.70	1.02	3.07	3.18	2.71	0.13
2	Chloroform	3.40 [8]	5.78	19.85	17.70	3.07	5.73	2.05	2.48	0.034
3	Toluene	3.23	4.87	18.21	18.05	1.43	2.05	3.23	2.55	0.11
4	Chlorobenzene	2.79	4.97	19.64	18.99	4.30	2.05	2.80	2.29	0.080
5	1,2-Dichloroethane	2.70	4.76	20.05	18.82	5.32	4.09	2.11	2.28	0.035
6	Tetrachloroethane	2.69 [8]	4.58	20.10	18.72	5.11	5.24	2.20	2.59	0.051
7	Carbon tetrachloride	2.40 [8]	4.08	17.70	17.70	0.00	0.00	5.69	5.05	0.32
8	Tetrahydrofuran	2.31 [8]	3.92	19.48	16.82	5.73	7.98	4.94	5.71	0.20
9	Benzene	1.95	2.79	18.82	18.31	1.02	2.05	3.61	2.88	0.12
10	Pyridine	0.87 [8]	1.47	21.69	18.93	8.8	5.93	5.50	6.01	0.24
11	*n*-Butyl acetate	0.80	1.36	17.39	15.69	3.68	6.34	5.19	5.77	0.26
12	4-Methyl-2-pentanone	0.77	1.30	17.19	15.33	6.14	4.09	5.75	6.35	0.42
13	Cyclohexane	0.53 [8]	0.91	16.78	16.74	0.00	0.00	6.19	5.75	0.42
14	1,4-Dioxane	0.50	0.85	20.48	19.23	1.84	8.59	5.64	5.74	0.27
15	Butanone	0.39 [8]	0.46	19.03	15.9	9.00	5.12	6.63	7.35	0.40
16	Methylpyrrolidone	0.17 [8]	0.17	22.86	17.90	12.28	7.16	8.86	9.53	0.76
17	Ethyl acetate	0.11 [8]	0.11	18.62	15.22	5.32	9.21	7.73	8.45	0.59
18	N,N-Dimethylacetamide	0.043	0.043	22.75	16.78	11.46	10.23	10.02	10.80	0.94
19	Acetone	0.041	0.041	20.25	15.51	10.44	6.96	8.66	9.44	0.56
20	Methyl acetate	0.033	0.033	19.64	15.46	5.93	10.02	8.11	8.86	0.53
21	Dimethyl formamide	0.023	0.023	24.86	17.43	13.71	11.25	12.17	12.91	1.2
22	Hexane	0.020	0.020	14.94	14.81	0.00	0.00	8.53	8.39	0.96
23	Iso-octanol	0.0041	0.0041	21.07	16.12	3.07	11.45	8.40	8.98	1.11
24	Ethanol	0.0036	0.0036	26.39	18.52	8.80	19.44	16.20	16.81	1.55
25	Isobutyl alcohol	0.0033	0.0033	22.10	15.14	5.73	15.95	13.36	14.05	1.67
26	Acetic acid	0.00	0.00	21.37	14.52	7.98	13.50	12.43	13.20	0.89
27	Isopropyl alcohol	0.00	0.00	23.53	15.75	6.14	16.36	13.33	14.01	1.37
28	Dimethyl sulfoxide	0.00	0.00	26.66	18.42	16.37	10.23	13.88	14.53	1.38

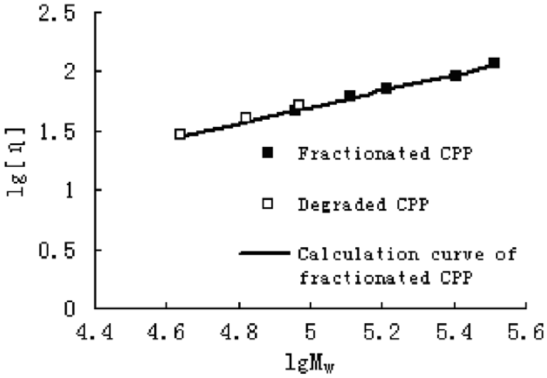

Figure 2. The relation between the undegraded solubility and the degraded solubility of CPP.

dispersion forces [3].

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

Hansen proposed an empirical equation that predicts the dissolvability of a polymer in an organic liquid [13]:

$$R_i = \sqrt{4(\delta_{ds} - \delta_{dp})^2 + (\delta_{ps} - \delta_{pp})^2 + (\delta_{hs} - \delta_{hp})^2} \tag{5}$$

where subscript index s and p designate the solvent and the polymer, respectively. The solute is at the center of the solubility sphere. Once the central coordinates of the solubility sphere, δ_{dp}, δ_{pp}, and δ_{hp} are determined and the interaction radius from its center of the solubility sphere to the points corresponding to solvents, R_i (also called solubility radius of the polymer in the corresponding solvent), are computed according to equation (5). The highest value of R_i in the good solvents is considered the radius of solubility sphere, R. For $R > R_i$, the polymer is soluble in a solvent and for $R < R_i$, the polymer is insoluble in a solvent.

The solubility parameters of solvents – δ_{ds}, δ_{ps}, δ_{hs} – are known. Giving a series of three-dimensional solubility parameters of the polymer, a fitting R can be obtained by an optimization method to enable all the points of soluble solvents to be inside the solubility sphere but all the points of insoluble solvents to be outside the solubility sphere in terms of equation (5). The solubility parameters corresponding to the fitting R are just the solubility parameters of the polymer by the optimization method. The results are obtained by a computer procedure.

According to the standard proposed in this article, for judging good and poor solvents as well as the three-dimensionalal solubility parameters of the solvents listed in table 2, the three-dimensional solubility parameters of CPP acquired by the optimization method are: $\delta_d = 18.00$ $(\mathrm{J\,cm^{-3}})^{1/2}$, $\delta_p = 4.00$ $(\mathrm{J\,cm^{-3}})^{1/2}$, $\delta_h = 4.00$ $(\mathrm{J\,cm^{-3}})^{1/2}$, $\delta = 18.87$ $(\mathrm{J\,cm^{-3}})^{1/2}$. The biggest value of R_i of the soluble solvents,

Table 3. The experimental results of solubility parameters of undegraded and degraded CPP. At 298.15 K (solution volume of toluene: 5 mL).

Sample	Concentration (g mL^{-1})	Hexane (mL)	Methanol (mL)	δ_{low} (J cm^{-3})$^{1/2}$	δ_{high} (J cm^{-3})$^{1/2}$	$\delta_{average}$ (J cm^{-3})$^{1/2}$	M_w
Undegraded CPP	0.0139	12.21	1.16	15.89	20.37	18.13	183,400
Degraded 20% CPP	0.0139	12.95	1.31	15.85	20.49	18.19	93,140
Degraded 10% CPP	0.0139	13.15	1.40	15.84	20.62	18.23	66,190
Degraded 1% CPP	0.0139	15.7	1.49	15.73	20.74	18.24	43,420

$R_{max} = 6.63$ (J cm^{-3})$^{1/2}$, is clearly less than the least value of the insoluble solvents, $R_{min} = 7.73$ (J cm^{-3})$^{1/2}$. All the points of soluble solvents are inside the solubility sphere and all the points of insoluble solvents are outside the solubility sphere. A clear boundary to judge good or bad solvents for CPP exists according to the values of R_i. The values of R_i of CPP in various solvents are listed in table 2.

3.4. *Verification of the total solubility parameters for CPP*

In order to verify the total solubility parameter obtained by optimization calculation, the turbidity method is used to determine the total solubility parameter for CPP. Samples are dissolved in toluene, and the solutions are respectively titrated to turbidity with hexane and methanol. The experimental results of the solubility parameters are listed in table 3.

From the trend listed in table 3, the volumes of hexane and methanol dropped into solution all increase with the decrease of molecular weights. This is consistent with the result that the solubility increases with the decrease of molecular weight shown in table 2. Both δ_{high} and δ_{low} all change while the average total solubility parameter is almost a constant. The total solubility parameter of CPP is 18.13 (J cm^{-3})$^{1/2}$, quite close to the value 18.87 (J cm^{-3})$^{1/2}$ calculated by the optimization method. The relative error is 3.9%. This indicates that the results of the three-dimensional solubility parameters acquired by optimization calculation are precise.

3.5. *The Flory–Huggins interaction parameters between CPP and its solvents*

Thomas Lindvig [14] suggested that the Flory–Huggins interaction parameters were related to the three-dimensional solubility parameters of polymers and solvents. The relation is as follows:

$$\chi_{12} = \alpha \frac{v_s}{RT}\left((\delta_{ds} - \delta_{dp})^2 + 0.25(\delta_{ps} - \delta_{pp})^2 + 0.25(\delta_{hs} - \delta_{hp})^2\right) \tag{6}$$

where v_s is the molar volume of a solvent. δ_{ds}, δ_{ps} and δ_{hs} are the solubility parameters of solvents and δ_{dp}, δ_{pp}, and δ_{hp} are the solubility parameters of CPP. Hansen [14] suggested to use this expression with $\alpha = 1$. However, Thomas Lindvig *et al.* found that the average absolute deviation is minimum with $\alpha = 0.6$ when they studied the activity coefficients of poly(butyl methacrylate) and poly(vinyl acetate). We discover that $\alpha = 1$ is suitable for CPP–solvent system.

Table 4. The solubility parameters of CPP as well as R_{max} and R_{min} obtained from different solubility boundaries $(J\,cm^{-3})^{1/2}$.

No.	The least solubility of soluble solvent	δ_d	δ_p	δ_h	δ	R_{min}	R_{max}
1	This article: 0.39 g/10 mL^{-1} solvent	18.00	4.00	4.00	18.87	7.73	6.63
2	Lieberman: 3% by weight	18.00	4.00	4.00	18.87	7.73	6.63
3	Hansen: 0.5 g/5 mL^{-1} solvent	18.20	3.50	3.50	18.86	5.74	5.71
4	Funasaka: 0.02 g/0.98 g^{-1} solvent	18.00	4.00	4.00	18.87	7.73	6.63
5	Wiehe: 0.1 g/25 mL^{-1} solvent	19.50	5.80	4.00	20.73	10.08	10.03

The calculated results of the interaction parameters between CPP and its solvents are also listed in table 2.

From the values of χ_{12}, 0.5 is the critical point to distinguish good solvents from bad solvents in the light of the proposed standard. The results in table 2 shows that when $\chi_{12} > 0.5$, CPP cannot dissolve and while $\chi_{12} < 0.5$, CPP can dissolve. The results are in accord with the standard of complete miscibility suggested by Flory–Huggins for polymers and solvents [15].

3.6. *Comparison between the standard proposed in this work and other standards for good or poor solvents*

Based on the relative solubility acquired in this work, the three-dimensional solubility parameters and the interaction radii of CPP can also be obtained by optimization calculation in terms of other judging standards. It is found that for different standards, good solvents are all inside the solubility sphere and poor solvents are all outside the solubility sphere. As expected, the three-dimensional solubility parameters and the interaction radii of CPP obtained by different standards are distinguishing. The result is listed in table 4.

Taking the undegraded CPP for example, the standard of solubility boundary proposed in this article is compared to the standards suggested by other researchers. The results are as follows:

(1) The solubility boundary used by Lieberman is 3% by weight. If the unit of solubility obtained in this work is converted into weight percent, the values of solubility of Butanone and Methylpyrrolidone, which are near 3%, are 4.37% and 1.54%, respectively. If the solubility of CPP in a solvent is larger than 4.37% or equal to 4.37%, the solvent is good and the solvent in which the solubility is less than 1.54% or equal to 1.54% is poor. The results of soluble and insoluble solvents along with the three-dimensional solubility parameters are the same as those of this article.

(2) The solubility boundary used by Funasaka is 0.02 g/0.98 g of solvent (2%). The results of good and poor solvents and the three-dimensional solubility parameters are also the same as that of this article.

(3) Wiehe regarded 4 g L^{-1} as the solubility boundary. After conversion of the unit, the concentration is 0.04 g/10 mL^{-1} of solvent. With Wiehe's standard, from No. 16 to No. 19, including acetone, listed in table 2 are all good solvents. But acetone is a bad solvent of CPP to be used as precipitating agent by which the product

of CPP grafted maleic anhydride (CPP-g-MAH) as well as ungrafted CPP are precipitated from toluene solution in the investigation of CPP-g-MAH. Moreover, the differences of δ, δ_d, as well as δ_p of CPP between Wiehe's standard and the others are obvious. The difference of δ between Wiehe's standard and the method of turbidity method (table 3) is apparent, too. Therefore, Wiehe's standard is too wide for judging good or poor solvents, and the corresponding three-dimensional solubility parameters are not precise.

(4) The solubility boundary applied by Hansen is $0.5\,\text{g}/5\,\text{mL}^{-1}$ of solvent. After conversion of the unit, the standard of solubility boundary is $1\,\text{g}/10\,\text{mL}^{-1}$ of solvent. No. 1–9 listed in table 2 are merely the good solvents. Although δ_d, δ_p, δ_h and δ obtained by Hansen's standard are quite close to the results of this article, the interaction radii (table 2) of CPP in various solvents are different. According to Hansen's standard, tetrahydrofuran locates the surface of the solubility sphere. However, the closer the solvent is to the surface of solubility sphere, the less is the solubility of CPP in it. In fact, tetrahydrofuran is a good solvent to be used to determine the molecular weight of CPP by gel permeation chromatography (GPC). Moreover, compared to 1.10 $(\text{J}\,\text{cm}^{-3})^{1/2}$, the difference between $R_{\max}$ and $R_{\min}$, which is obtained from the standard proposed in this article, but according to Hansen's standard, the difference is only 0.03 $(\text{J}\,\text{cm}^{-3})^{1/2}$, which is too close to distinguish the good and poor solvents. Accordingly, Hansen's standard is narrow for judging good and poor solvents.

From the comparison described above, the calculated solubility parameter of CPP is reasonable and the standard of solubility boundary proposed in this article for judging the good and poor solvents of CPP is feasible. This judging method can supply a reference for other polymers.

4. Conclusion

Ultrasonic degradation of CPP and its solubility parameters were studied systematically. The following conclusions can be drawn from the work:

(1) The chlorine content, structure of molecules as well as the configuration of molecules in toluene are the same as that of CPP. Therefore, that the Mark–Houwink equation obtained from fractional precipitations is also suitable for degraded CPP enlarges its application range.

(2) Through the systematical investigation on the solubility of CPP and degraded CPP, it is found that for a good solvent, the solubility of degraded sample is larger than and is proportional to the solubility of undegraded sample. Consequently, an objective new standard for judging good and poor solvents of CPP is proposed. The standard is that solvents in which the solubility increases with the decrease of molecular weight are good solvents and the solvents in which the solubility does not change with the molecular weight are insoluble ones. The results obtained by the proposed standard are consistent with the standard of complete miscibility suggested by Flory–Huggins for polymers and solvents as well as the practical good and bad solvents of CPP. This standard may provide a reference for other polymers.

(3) According to the proposed standard, the three-dimensional solubility parameters and the total solubility parameter of CPP acquired by optimization calculation are: $\delta_d = 18.00$ $(\mathrm{J\,cm^{-3}})^{1/2}$, $\delta_p = 4.00$ $(\mathrm{J\,cm^{-3}})^{1/2}$, $\delta_h = 4.00$ $(\mathrm{J\,cm^{-3}})^{1/2}$, $\delta = 18.87$ $(\mathrm{J\,cm^{-3}})^{1/2}$. They are verified by the turbidity method. The calculated solubility parameters are reasonable.

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