SPMC Technical Review EN

Utilization of KJCMPA®-100

− As a solvent for polymer analysis −

SEIKO PMC CORPORATION
Technology Division Mari Nakagawa
Koya Uchiyama
Toshio Hokajo

KJ Chemicals Corporation
Business Headquarters Hideki Masuda

1. Introduction

Polymers are used in a variety of fields, and their composition, structure, and molecular weight have significant effects on polymer properties. Therefore, polymer analysis is essential to elucidate the origin of the differences in the properties and functions of polymers or to obtain a guideline in the structural design.

Finding a good solvent is important for molecular weight and NMR measurements because accurate analysis is not possible unless the polymer is dissolved in the solvent completely. If there were universal solvent that could dissolve any polymers, such situation would be desirable. However, the solubilities of polymers to a solvent are different due to differences in their structures and functional groups. We usually use THF (tetrahydrofuran), DMF (dimethylformamide), or DMSO (dimethylsulfoxide) for polymer analysis in dependence on its solubility.

We noticed that KJCMPA®-100 from our group company KJ Chemicals, Inc. better dissolves the polymers that are poorly soluble in the general-purpose solvents. We utilize this solvent for polymer analysis.

In this report, we first describe the features of KJCMPA®-100, followed by Molecular weight and NMR measurements of the polymers using the solvent. Lastly, the excellent ability of this solvent to dissolve solutes is demonstrated using Hansen Solubility Parameters (HSP).

2. KJCMPA®-100

KJ Chemicals utilizes their unique synthetic methodologies of acrylamide derivatives to manufacture and sell a variety of amide compounds including dimethylacrylamide (DMAA®) and acryloylmorpholine (ACMO®). KJCMPA®-100 is an amphiphilic functional solvent (β-alkoxypropanamide analogues) with amide and alkyl groups in the molecule. They have put it on the market, and are looking for potential customers. The substance name of

Table 1. CAS No. and registration

	KJCMPA®-100
CAS No.	53185-52-7
Registered in	Japan Korea Taiwan USA Europe

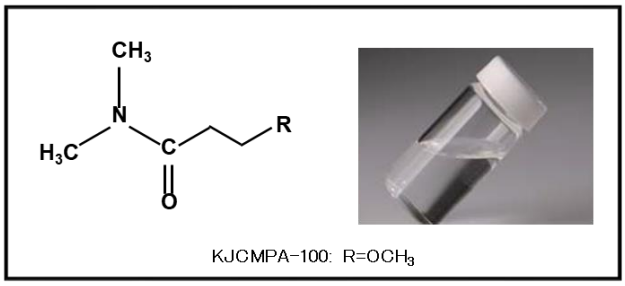

Figure 1. Structure and appearance

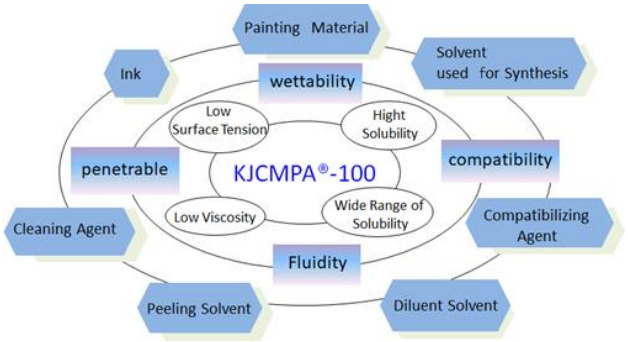

Figure 2. Features and applications of KJCMPA®-100

KJCMPA®-100 is 3-methoxy-N,N-dimethyl-propanamide, and its structural formula is in Figure 1.

KJCMPA®-100 is a colorless solution (melting point: -49° C, viscosity: 2.3 mPa-s (20° C)) and is mainly used as a solvent. As an amphiphilic substance with amide and alkyl groups in its molecule, it can dissolve substances with a wide range of polarity. This solvent can even solubilize least soluble polymers such as fluorinated polymers and polyamides.

Polyimide and polyamide are widely used as insulating materials, but their high crystallinity makes it difficult to completely dissolve them in common solvents. NMP (N-methylpyrrolidone) and DMF（N,N-dimethylformamide) are usually used to dissolve them. However, it is warned that these solvents may pose safety and environmental concerns. On the other hand, KJCMPA®-100 has been proven to be a safe substance with no teratogenicity and low skin irritation.

KJCMPA®-100 could also be used as adhesion-enhancer for inkjet (IJ) inks, film-forming aids for water-based coatings, detergents, and release agents as well as in the applications in the manufacturing processes of pharmaceutical and agrochemical products. Although KJCMPA®-100 and NMP have similar boiling points and viscosity, KJCMPA®-100 shows a lower contact angle and is generally twice as wettable on substrates as NMP. For example, if KJCMPA®-100 is used as a solvent for inkjet inks, it is expected to improve the discharge stability of printers, and the storage stability and printability of ink. KJCMPA®-100 is also expected to be used in various fields as a solvent that is safe and useful in dissolving polymers.

3. Characteristics and polymer solubilities of various analytical solvents

In addition to being a good solvent, the followings are important criteria required to be recognized as a good analytical solvent:

- not reactive with the sample
- miscible with other solvents
- low toxicity to human body
- inexpensive and easily obtainable

Table 2. Physical properties of solvents

	KJCMPA®-100	NMP	THF	DMF	DMSO
Boiling Point (℃)	216	204	66	153	189
Melting Point（℃）	-49	-24	-108.4	-61	19
Density (20℃：g/cm^3)	0.99	1.03	0.89	0.94	1.1
Viscosity (20℃：mPa・s)	2.3	1.8	0.48 (25℃)	0.92	1.996
Refractive Index	1.45	1.47	1.41	1.43	1.48
Surface Tension (23℃：mN/m)	34.2	38.6	26.4 (25℃)	—	44※1
IARC Carcinogenicity Classification category	—	—	Group 2B	Group 2A	—

※1: Temperature is unknown

Table 2 summarizes the physical properties of KJCMPA®-100 and common solvents used in polymer analysis.

Solvents with a high melting point such as DMSO can freeze indoors during winter, which makes the handling poor. On the other hand, KJCMPA®-100 does not freeze under the same condition. Furthermore, comparably high boiling point of KJCMPA®-100 makes it suitable for dissolving polymers at elevated temperatures.

Table 3 shows the solubilities of various polymers in

Table 3. Solubility of polymers in solvents

	KJCMPA®-100	THF	DMF	DMSO
Polystyrene (pSt)	○	○	○	×
Poly (methyl methacrylate) (pMMA）	○	○	○	○
Styrene-maleic anhydride copolymers	○	○	○	○
Polycarbonate	○	○	△	×
Polyvinyl acetate	○	○	○	○
Polyether imide	○	×	△	×
Pullulan	×	×	○	○
Starch	×	×	×	○
Polyvinyl alcohol	×	×	×	×
Polyvinylidene fluoride	○	△	△	×
Polychlorotrifluoroethylene	×	×	×	×
Poly tetrafluoro ethylene（PTFE）	×	×	×	×
Polyacetal resin	×	×	×	×
tetrafluoroethylene-ethylene copolymer	×	×	×	×
polypropylene (PP)	×	×	×	×
polyethylene glycol (PEG)	○	○	○	○
polyphenylene sulfide	×	×	×	×
polyether ether ketone (PEEK)	△	×	×	×
Nylon 6	△	×	×	×
Nylon 66	△	×	×	×
Nylon 12	○	×	×	×
polyimide	×	×	×	×
polyamide imide (PAI)	○	×	△	△
polyether sulfone	○	×	○	○
thermoplastic polyurethane (TPU)	○	○	○	○
polyacrylamide	×	×	×	○
Number of polymers dissolved	12	7	8	9

concentration：0.3%　○：soluble　△：partially soluble・swell　×：insoluble

each solvent. The solubilities shown in Table 3 are just an example; even if the composition does not differ much, the polymer may not dissolve in the solvent depending on the molecular weight, the branching, and the monomer sequence of the polymer.

4. Molecular weight measurement

Molecular weight is one of the important indicators to assess the synthesis method and estimate the physical properties of polymers. Generally, molecular weight is measured by size exclusion chromatography (SEC). There are two types of molecular weight measurement methods. One is Relative Molecular Weight Measurement using a differential refractive index (RI) detector or ultraviolet-visible spectroscopy (UV-Vis) detector to generate a calibration curve for a reference material with known molecular weight. The other method is Absolute Molecular Weight Measurement using a self-calibration curve obtained from a multi-angle light scattering (MALS) detector. Eluent for the measurements should be chosen that does not give ghost peaks that overlap with the polymer peaks. Figure 3 shows the chromatogram of KJCMPA®-100 and polymer (polycarbonate) using RI detector. It is suitable as an eluent for molecular weight determination of polymers (polycarbonate).

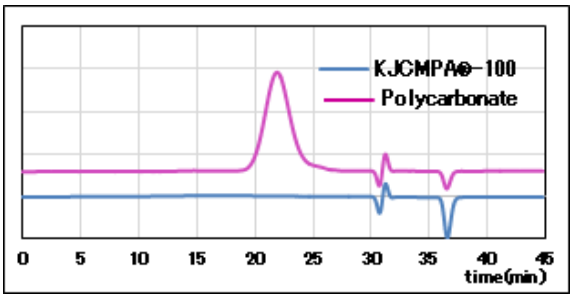

Figure 3. RI comparison of polycarbonate and KJCMPA®-100

《Measurement Conditions》
Analysis Time：45min
Column Temperature：70℃
Column：Tosoh TSKgel α-M×2
RI Detector：Shodex RI-101
MALS：Wyatt DAWN8+
LC：Shimadzu Prominence Series

4-1. Relative molecular weight

Reference material is used to determine the relative molecular weight of polymers. More accurate molecular weight can be obtained by using a reference substance having a structure as close as possible to the polymer to be measured. KJCMPA®-100 can dissolve polystyrene (pSt) and polymethyl methacrylate (pMMA), which are used as reference. Figure 4 shows a calibration curve drawn with pSt or pMMA using KJCMPA®-100 as the eluent.

With KJCMPA®-100, both pSt and pMMA draw their calibration curves with a gentle slope in the molecular weight range of 1,000 to 1,000,000. Either of these calibration curves can be used as SEC calibration curves.

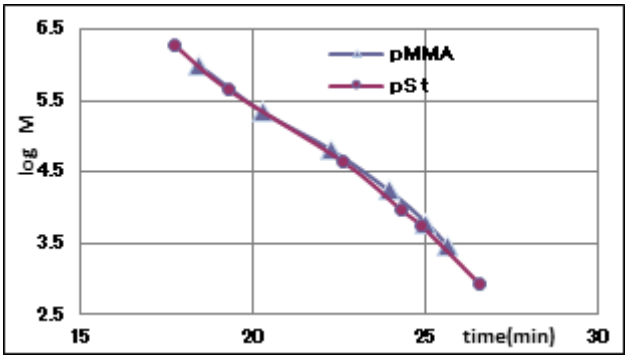

Figure 4. pMMA, pSt calibration curve in KJCMPA®-100

4-2. Absolute molecular weight

Molecular weight measurements using the MALS detector can determine the absolute molecular weight, molecular size, and second virial coefficient of various polymers by static light scattering. It also provides information on polymer branching introduced by cross-linking agents and graft polymerization.

Relative molecular weight measurement is useful for comparing polymers of the same composition and

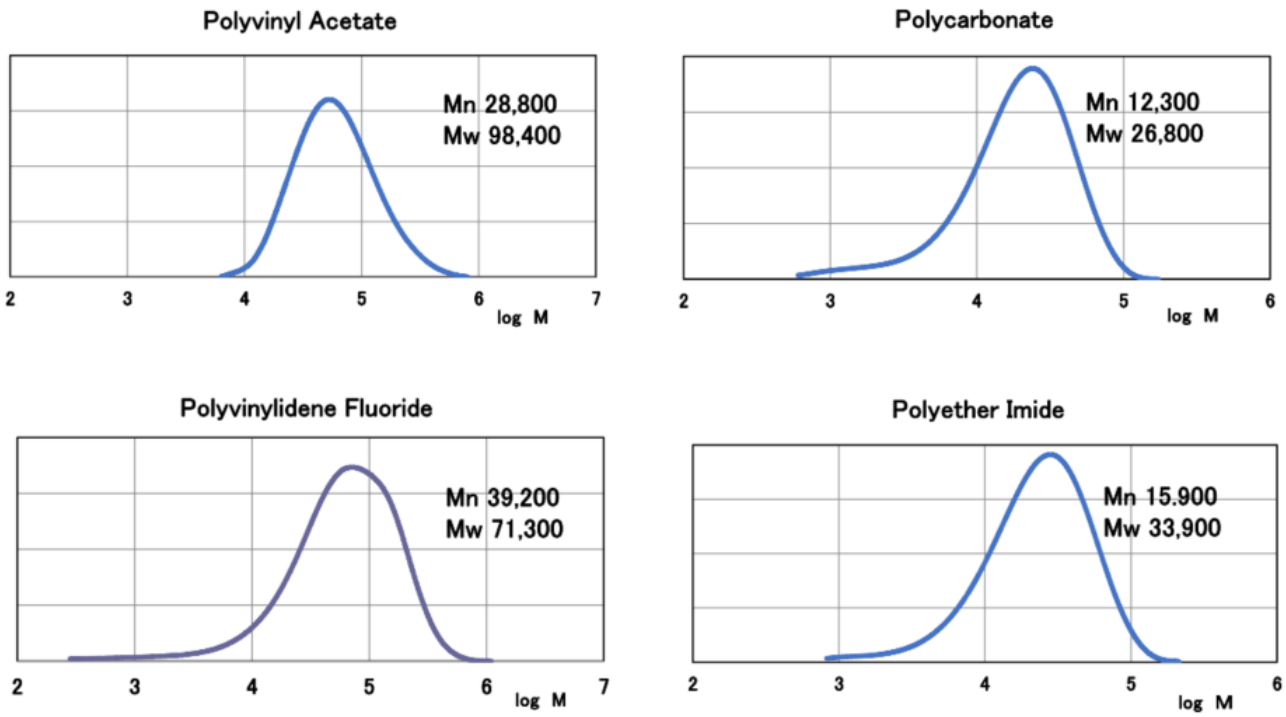

Figure 5. Absolute molecular weight distribution of polymers in KJCMPA®-100

structure. However, if the molecular structures of the polymer and the reference material is significantly different, the measured molecular weight deviates from the real value in a large extent. In the meanwhile, absolute molecular weight measurement calculates the true molecular weight by creating a self-calibration curve, which allows direct comparison of molecular weight of polymers with different compositions and structures.

Differential refractive index increment, dn/dc, is needed to calculate the absolute molecular weight. RI detector is used for the actual dn/dc measurement. Figure 5 shows the absolute molecular weight distribution of several polymers with KJCMPA®-100 as the eluent. Although the composition and structure of these polymers are different, absolute molecular weight measurement allows the direct comparison of the molecular weight distribution. As can be seen in Figure 5, KJCMPA®-100 can be used as an eluent for SEC-MALS measurements.

5. NMR

NMR spectroscopy is a useful tool for determining the composition and structure of polymers. In the measurement, deuterated solvents are usually used to dissolve samples.

However, in cases that

・it is preferable to measuring as it is due to its instability.

・it is time-consuming to replace the solvent.

・the sample is only soluble in a limited choice of solvent.

non-deuterated solvents can be used for the measurement.

The result of 1H NMR measurement of polyvinylidene fluoride in KJCMPA®-100 is shown in Figure 6. Under normal measurement conditions, the signals from polyvinylidene fluoride are interfered by the signals from KJCMPA®-100. However, the diffusion filter method can eliminate signals from the components with

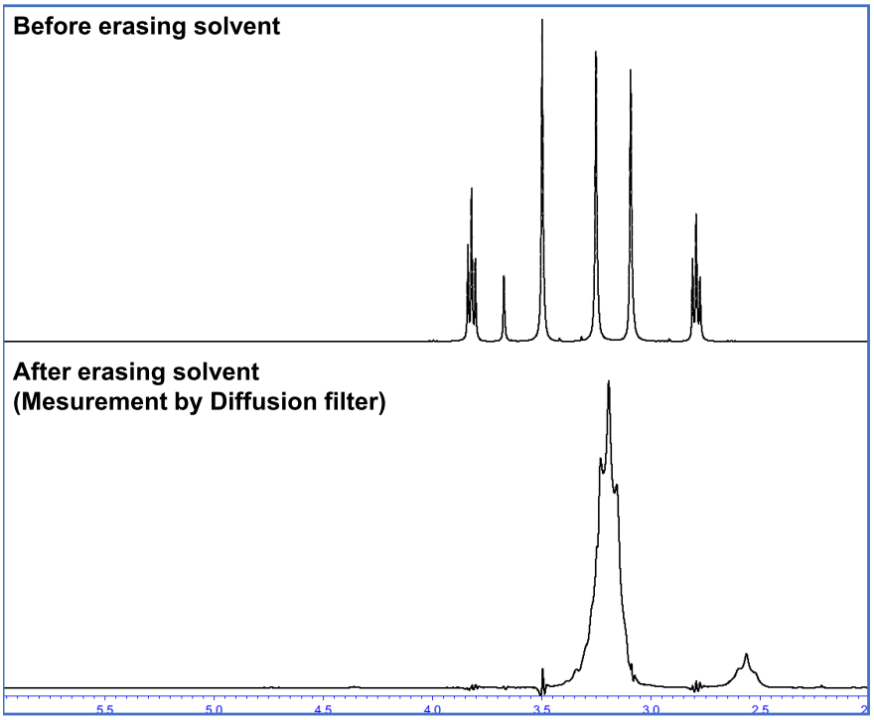

Figure 6. Comparison of NMR spectra with or without diffusion filter

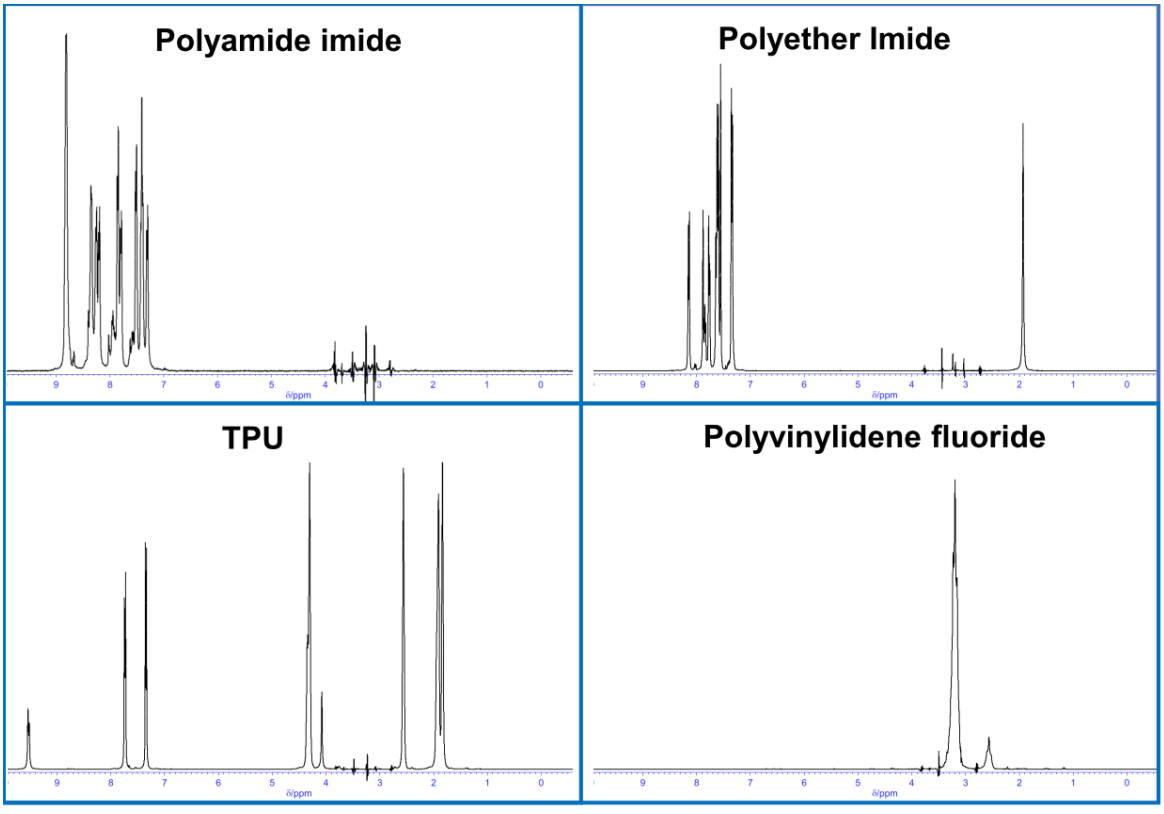

Figure7. 1H-NMR spectra of polymers

《Measurement conditions》

^{1}H-NMR (diffusion filter method)

Sample concentration 2%

a large diffusion coefficient (KJCMPA®-100) to leave the signals almost exclusively from polyvinylidene fluoride.

Figure 7 shows NMR spectra with this technique: the KJCMPA®-100 hardly interferes with the polymer signals, and clear spectra are obtained.

The diffusion filter method has also been applied to two-dimensional NMR spectroscopy.2) The combination of this technique and KJCMPA®-100 is expected to make the detailed structural analyses of poorly soluble polymers possible (identification of unknown structure and end structures).

6. Hansen Solubility Parameters

We have mentioned that KJCMPA®-100 is a good solvent in SEC and NMR measurements. It also allowed us to determine the structure, composition, and molecular weight of polymers that could not be analyzed otherwise. To evaluate the solubility of such polymers Hansen Solubility Parameters (HSP) is used. The HSP is a value used to predict the solubility of polymers and resins based on the idea that "two substances with similar intermolecular interactions tend to dissolve each other". HSP consists of three parameters shown in Figure 8. These parameters for common solvents and KJCMPA®-100 are shown in Table 4. Next, the solubility of the polymers listed in Table 3 was discussed by drawing a Hansen solubility sphere. The HSPs for about 30 polymers were

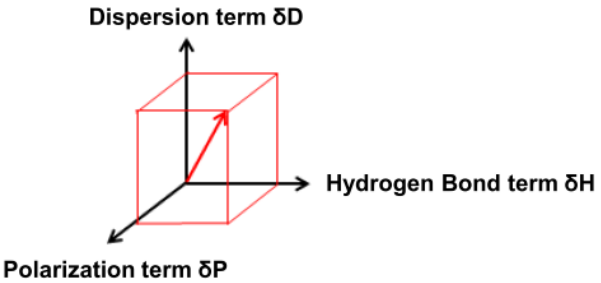

Figure 8. Diagram representing HSP

Table 4. Calculated value by HSPiP version 4.0.04 Y-MB

	δD	δP	δH	δ(total)
KJCMPA®-100	17.2	10.9	9.5	22.5
NMP	18.1	10.3	6.6	21.8
THF	16.7	4.9	5.5	18.3
DMF	17	13.3	10.9	24.2
DMSO	17.4	14.3	7.3	23.7
Acetone	15.5	10.4	7	19.9
Methanol	14.7	12.3	22.3	29.4
Ethanol	15.8	8.8	19.4	26.5
Acetonitrile	15.3	18	6.1	24.4

calculated and plotted on the coordinates for each the solvent. Most of the plots gathered near the center of the sphere (see Figure 9 on the next page). These spheres are made to contain almost all of the dissolved polymers. Since δD values for these solvents do not differ significantly, we look for the difference in δP and δH. In comparison of them, KJCMPA®-100 is considered to have properties between those of THF and DMF.

The larger the sphere, the more polymers that the solvent can dissolve. To elucidate the concept, the combinations of δD-δP, δD-δH, and δH-δP are expressed on two-dimensional coordinates. On the coordinates for THF the circle is small, which means that only a smaller number of polymers are soluble in THF. In contrast, DMF and DMSO have large dissolution spheres, but many polymers in the sphere do not dissolve in them. If all the insoluble polymers are removed from the coordinates, the spheres are flattened rather than spherical. This means that there are strong preferences of the solvents for the certain types of polymers to dissolve. The sphere shows that KJCMPA®-100 dissolves a wider variety of the polymers because the size of the sphere is large and smaller number of insoluble polymers are in the sphere.

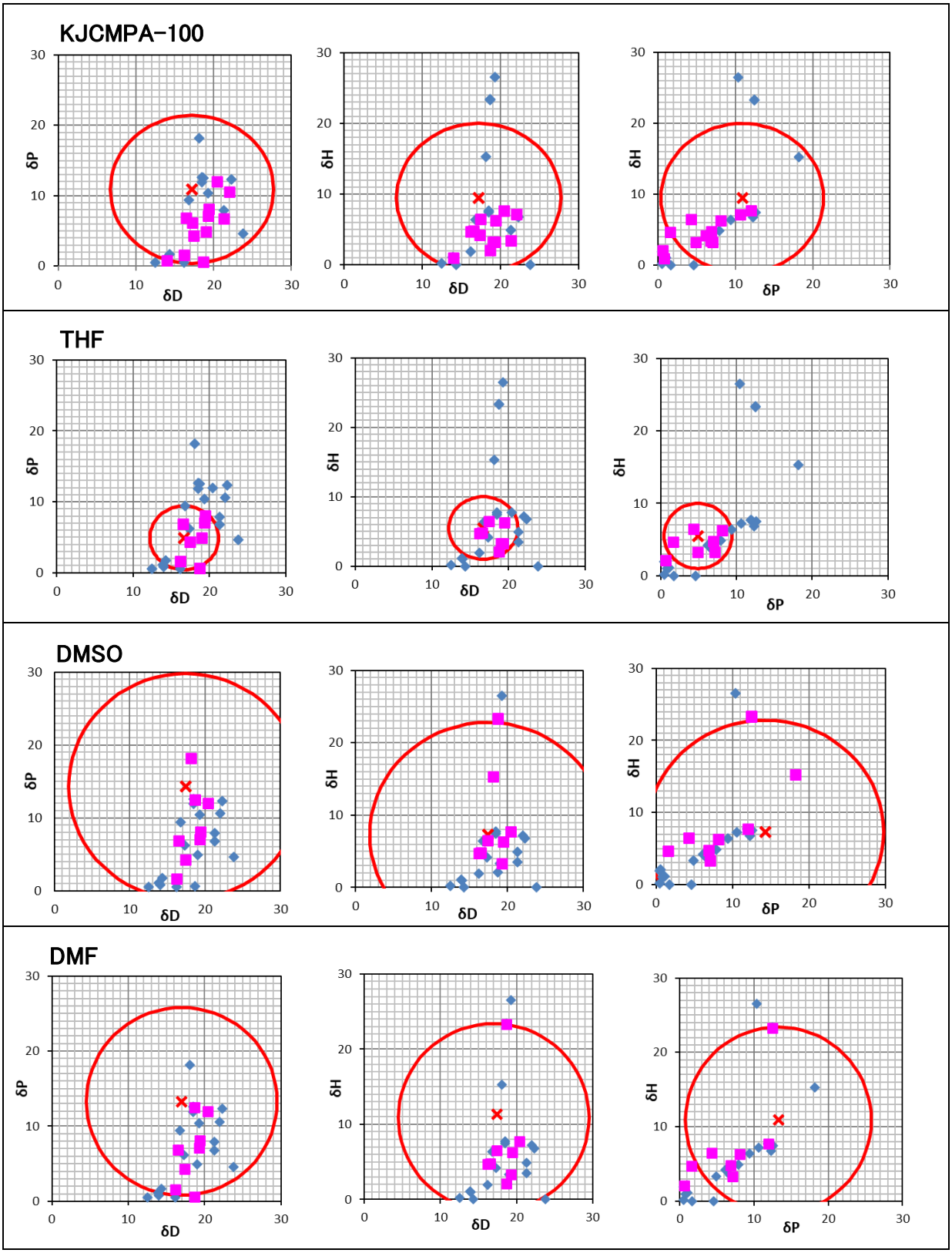

Figure 9. Hansen soluble sphere in each solvent

7. Conclusion

KJCMPA®-100 was demonstrated to be a good solvent for polymers with various degree of polarities and those that are poorly soluble in common solvents. Its excellent dissolving ability can be recognized using the HSP. KJCMPA®-100 has already been used in various applications as a solvent that is safe, easy to handle, and exhibits excellent ability to dissolve various substances. In this study, KJCMPA®-100 was shown to be extremely effective as a solvent for SEC and NMR Profile measurements.

We believe that the use of KJCMPA®-100 as a solvent for analysis will enable the study of various polymers and expand the field of R&D of products.

＜References＞

1) M Nakagawa, T Hokajo, The abstracts of the 24th Polymer Analysis and Characterization Symposium

2) M. Oouchi, J. Ukawa, Y. Ishii, H. Maeda, Biomacromolecules 2019, 20,1394-140

SEIKO PMC CORPORATION
Technology Division
Technical Analysis Group
Assistant manager
Mari Nakagawa

SEIKO PMC CORPORATION
Technology Division
Technical Analysis Group
Koya Uchiyama

SEIKO PMC CORPORATION
Technology Division
Technical Analysis Group
Manager
Toshio Hokajo

KJ CHEMICALS CORPORATION
Business Headquarters
Director
Hideki Masuda