Abstract: In this study, a 2-pack isocyanate curing waterborne paint (without organic solvents) encapsulating dibutyltin dilaurate (hereinafter, DBTL) in nonionic surfactant micelles with an hydrophilic–lipophilic balance of 13–14 in advance releases DBTL when the micelles are collapsed at 80 °C or higher, whereby the curing progresses rapidly. On the other hand, the viscosity levels of the paint before and after being left at 40 °C for 1 h are almost the same. Organic solvents are mandatory for waterborne paints to provide paint and film properties, but they might collapse the micelles when they are formulated in the paint. In this study, we investigate whether the abovementioned paint containing organic solvents can develop switching functionality in terms of maintaining the storage stability at 40 °C and expressing a catalytic function at 80 °C to progress the curing. As a result, we find that if the solubility of the organic solvent in water at 20 °C is at least 10 g/100 mL and the boiling point is ≤200 °C, both curing and storage stability can be achieved.

Keywords: catalyst; non-ionic surfactant; micelle; waterborne paint

1. Introduction

Thermosetting resins used in automotive body paint mainly consist of acrylic polymers containing hydroxyl groups and curing agents, such as isocyanate groups and melamine resins, to ensure coating performance. Although it is known that the reaction between an acrylic polymer and isocyanate proceeds slowly, even at room temperature [1], in the actual coating process, to reduce the process length and to complete the curing reaction, baking under high temperatures (140 °C to 160 °C) for a short time after spray coating is utilized. However, automotive body manufacturers are investigating the possibility of lowering the baking temperature to reduce carbon dioxide emissions and save costs [2]. Furthermore, the use of resin in parts on the outer panel is also being investigated to reduce vehicle weight [3]. Achieving this involves painting and baking the steel plate (on the body) and the resin (on the bumper) together to reduce costs and match the colors of the body and bumper [4]. In this case, it is necessary to ensure the baking temperature is low enough to avoid deformation of the resin, which is an important consideration for automotive body manufacturers.

The automobile body painting process consists of three coating layers, namely a primer surfercer, base coat, and clear coat, on an electrodeposited steel sheet. Although both the primer surfercer and the base coat comprise a curing system mainly composed of acrylic polyol and melamine resin [5], low-temperature (100 °C) baking is very difficult for melamine resin curing systems. Accordingly, the use of isocyanate as a curing agent is necessary. Meanwhile, the clear coat, which forms the uppermost layer, is a curing system mainly consisting of acrylic polyol and isocyanate or epoxy–carboxy functional acrylic resins [6]. In the acrylic polyol and isocyanate curing systems, an increased amount of catalyst such as dibutyltin dilaurate (DBTDL) makes it possible to lower the baking temperature to 100 °C, while decreasing the time taken for curing [7]; however, while enabling low-temperature baking, the reactivity at room temperature also increases, meaning the
storage stability of the paint may deteriorate. To avoid this problem, the use of curing agents in which the isocyanate is masked with a blocking agent such as dimethyl pyrazole or methyl ketoxime has been considered [8]; however, this is undesirable because the abovementioned blocking agent volatilizes into the air during the baking process when released, which may have an adverse effect on the environment.

In this study, we investigate the possibility of creating a so-called “switching catalyst” to ensure sufficient curability by developing the catalytic function at 80 °C in a 2-pack isocyanate curing system, while enabling storage stability and pot life by not developing the catalytic function at low temperatures of ≤40 °C. Various techniques for encapsulating catalysts in microcapsules and inclusion compounds have been reported [9–15]. We focus on the possibility of encapsulating catalysts in surfactant micelles. As a result, it is found that the 2-pack isocyanate waterborne paint (without organic solvents) containing DBTL and encapsulated in advance in nonionic surfactant micelles with hydrophilic–lipophilic balance of 13–14 releases DBTL with the collapse of the micelles at 80 °C or higher for the rapid progress of curing, while at the same time the viscosity levels of the paint before and after standing at 40 °C for 1 h remain almost the same [16].

Numerous organic solvents are used in waterborne paints for automobile bodies to ensure paint stability and improve the leveling of the coating film [17]; however, they might collapse the micelles, meaning the switching functionality of the catalyst is deactivated when they are formulated in the paint. In this study, we examine whether the catalytic function of the coating will appear at 80 °C while maintaining storage stability at 40 °C in the abovedescribed coating system containing various organic solvents.

Figure 1 shows a catalyst that exhibits switching functionality. In this study, we first investigate whether it is possible to isolate (deactivate) the catalyst in micelles in paints and low-temperature coatings and then achieve a switching function to activate the catalyst following the collapse of the micelles above a certain temperature, based on the curing behavior of the paint film and the storage stability of the paint. Subsequently, we examine the changes in the molecular weights of the micelles when the catalyst is added using the static light scattering method. Finally, we discuss the mechanism involved in the appearance of the switching functionality with different organic solvents based on the results.

![Figure 1. A catalyst encapsulated in a micelle in surfactant solution.](image)

2. Materials and Methods

2.1. Preparation of Paint

2.1.1. Paint without Organic Solvents

The oleic-acid-type surfactant Nonion E-212 (a product of Nichiyu, Tokyo, Japan; hereafter referred to as E-212) was used. It can activate the catalytic function at approximately 80 °C, as previously reported [16], as a nonionic surfactant that develops a switching function in the production and extinction of micelles. This was dissolved in deionized water to a concentration of 20 wt% to form a transparent aqueous solution. DBTL was...
added to the solution at a concentration of 2 wt%. After addition, the aqueous solution was heated to 60 °C and stirred until uniform DBTL was uniformly dispersed.

Paints were prepared by mixing the above aqueous solution with an acrylic emulsion and polyisocyanate. The acrylic emulsion [16] with a glass transition temperature of 20 °C (calculated value obtained from the glass transition temperature of acrylic monomer) and a hydroxyl value of 150 (same as above) was synthesized. A water-dispersible polyisocyanate Burnock DNW5500 (a product of DIC Corporation, Tokyo, Japan) was mixed to obtain a 1:1 molar ratio of hydroxyl groups to isocyanate groups in the acrylic emulsion. Furthermore, the abovementioned surfactant–DBTL solution was added to attain a DBTL concentration of 0.1 wt% in the paint, then Voncoat HV-E (DIC Corporation) and dimethylaminoethanol (product of Wako Junyaku Kogyo, Tokyo, Japan) were added as the alkaline thickener and neutralizer, respectively, and the mixture was used as the sample for evaluation (hereinafter referred to as E212–DBTL). A sample without the surfactant–DBTL solution (hereafter referred to as DBTL-free) was also prepared in the same manner. Moreover, direct addition of the acrylic emulsion was attempted without adding DBTL to the surfactant, but since DBTL is a hydrophobic substance, uniform dispersion was difficult, so the water in the acrylic emulsion was removed in a vacuum dryer under room temperature. The samples were prepared by adding Burnock DNW5500, acetone, and DBTL (the concentration of DBTL in the paint was 0.1 wt%, hereafter referred to as DBTL (directly added)).

2.1.2. Paints Containing Organic Solvents

Paints were also prepared by adding 10 wt% of organic solvents with different water solubility levels and boiling points to E212–DBTL (Table 1). All the organic solvents in Table 1 are commonly used in waterborne paints. The water solubility values in Table 1 indicate the amount of organic solvent dissolved in 100 mL of deionized water, and the state of dissolution was visually judged.

| Abbreviation of Organic Solvent | Chemical Name                          | Water Solubility (g/100 mL, 20 °C) | Boiling Point (°C) [18] | Abbreviation of Paint |
|---------------------------------|----------------------------------------|-----------------------------------|-------------------------|-----------------------|
| iPrOH                           | 2-propanol                             | ≥10                               | 83                      | E212–DBTL(iPrOH)      |
| PrOH                            | 1-propanol                             | >10                               | 97                      | E212–DBTL(PrOH)       |
| BuOH                            | 1-butanol                              | 10                                | 118                     | E212–DBTL(BuOH)       |
| 2EhOH                           | 2-ethylhexanol                         | ≤1                                | 184                     | E212–DBTL(2EhOH)      |
| PrM                             | 1-methoxy-2-propanol                  | >10                               | 120                     | E212–DBTL(PrM)        |
| EtB                             | ethylene glycol mono butyl ether       | ≥10                               | 171                     | E212–DBTL(EtB)        |
| Et2Eh                           | ethylene glycol 2-ethylhexyl ether     | ≤1                                | 229                     | E212–DBTL(Et2Eh)      |

2.2. Measurement of Paint Curing Behavior

The above paint was applied to a 40 mm × 50 mm stainless steel plate (thickness 0.5 mm) to attain a film thickness of 35 ± 5 µm after baking. Specifically, the stainless steel plate was placed on a horizontal stand, 70-µm-thick adhesive tape was attached to an area about 5 mm from each of the two opposite ends of the stainless steel plate, a knife with a straight edge was slid over the tape, and the paint was applied to the gap between the stainless steel plate and the knife edge.

Ten minutes after forming the coating made of the above paint on the stainless steel plate, the relative storage modulus (E’r) of the coating was measured for curing conditions of 70 to 100 °C by increments of 10 °C. The measurement was performed using a rigid-body pendulum-type tester (RPT-5000, a product of A&D Corporation, Tokyo, Japan) equipped with a circular pendulum measuring 74 mm in diameter fitted with a knife edge with a blade angle of 40°. The temperature program during measurement was set to increase the temperature from room temperature (20 °C) to the baking temperature at a rate of 20 °C/min, then to maintain the curing temperature. The measurement was continued for at least 15 min after the inflection point mentioned below.
Plotting the measured relative storage modulus ($E'$) against time, we can see that the curve changes from a downward convex curve to an upward convex curve according to the progress of time (hereafter, this point of change is called the “inflection point”) (Figure 2).

![Figure 2. Measurement example of the relative storage modulus of a paint versus time.](image)

Equation (1) [19] was obtained for the period 15 min from the inflection point:

$$E' = A[1 - \exp\{k(t - td)\}]$$

(1)

where $A$ is a constant, $k$ is the curing speed constant, $t$ is the time, $td$ is the start time for curing, and $k$ is determined using the nonlinear least-squares method. The larger the $k$ value, the faster the curing progresses.

### 2.3. Measurement of Changes in Molecular Weight of Micelles

Static light scattering measurements were performed using a DLS-8000 dynamic light scattering spectrophotometer (a product of Otsuka Denshi, Osaka, Japan) to investigate the changes in the molecular weights of micelles. The samples were prepared as follows. E-212 was dissolved in deionized water to a concentration of 20 wt% to produce a transparent aqueous solution. DBTL was added to this solution at a concentration of 4 wt%. After addition, the aqueous solution was heated to 40 °C and stirred until the curing catalyst was uniformly dispersed. The solution was then diluted with deionized water to obtain surfactant concentrations of 0.025, 0.050, and 0.075 wt%. Then, PrOH and 2EhOH at 0.2 wt% were added to each of these to prepare samples. The deionized water was previously filtered through a 0.1 µm filter.

The measurements were performed under the following conditions. The temperature was increased in the order of 25, 40, and 50 °C. The measurement angles were set at 40, 50, 60, 70, 80, 90, 120, and 150°. The measurement time was 16 s, the number of integration cycles was 100 times, with 1 repetition.

The scattering intensity data obtained at each concentration and angle were analyzed using Zimm’s square root plot [20] to obtain the molecular weight ($M_W$). The $dn/dc$ required for the calculation of $M_W$ was determined from the refractive indices at each concentration with a DRM-3000 high-sensitivity differential refractometer (a product of Otsuka Denshi, Osaka, Japan; E-212–DBTL-free: 0.0282 mL/g). The sample with DBTL was not measured but there was no significant change presumed in the value; therefore, the sample without DBTL was used. Water at 25 °C with a refractive index of 1.33 and viscosity of 0.89 mPa s was used as a solvent.
2.4. Evaluation of Storage Stability

The above paint was left in an oven at 40 °C for 1 h and the viscosity was measured using an ARES-G2 rheometer (a product of T.A. Instruments, Tokyo, Japan) before and after the paint was placed in the oven. The measurement conditions were: temperature: 25.0 ± 0.1 °C; shear rate: 1000 s\(^{-1}\); geometry: 25 mm diameter cone plate; rad angle: 0.04; gap: 50 μm. DBTL (directly added) was not measured because of gelation after being left in the oven.

3. Results and Discussion

3.1. Curing Behavior of Paint

3.1.1. Temperature Dependence of k for the Paint without Organic Solvent

Figure 3 shows the relationship between the k value (closed circle) of E212–DBTL and the curing temperature, together with the k value (open triangle) for DBTL-free and the k value (open circle) for DBTL (directly added). As shown in Figure 3, k increased with increases in curing temperature for both DBTL-free and DBTL (directly added). Further, at any curing temperature, the k value for DBTL (directly added) was found to be greater than for DBTL-free. The value of k was much lower for DBTL (directly added) compared to E212–DBTL, with differences of up to 70 °C, but increased rapidly above 70 °C; at 100 °C, k was almost equal to that for DBTL (directly added) and gradual switching was confirmed. This may have been due to the fact that the catalytic function is inactive until 70 °C because a great part of DBTL is restrained in the micelles, while the catalytic function becomes active above 70 °C due to the collapse of micelles.

![Figure 3. Relationship between the curing speed constant (k) and curing temperature.](image)

3.1.2. Temperature Dependence of k for the Paint Containing Organic Solvent

The relationship between the k value (closed triangle) of E212–DBTL(PrOH) and curing temperature is shown in Figure 4, together with the k value (closed square) of E212–DBTL(2EhOH) associated with data from Figure 3. The addition of PrOH resulted in increased k at 70–80 °C. This may have been due to the activation of the catalytic function by the partial collapse of the micelles upon PrOH addition. When 2EhOH is added, k at 70–80 °C increased greatly compared to PrOH and was essentially the same as for DBTL (directly added). This can be explained by the fact that since 2EhOH is less soluble in water...
than PrOH, it can be more easily incorporated into the micelles, resulting in DBTL release. Furthermore, the higher boiling point of the organic solvent may cause volatilization even when heating, facilitating its incorporation into the micelles. In Section 3.2, the Mw of the micelles in the above samples will be investigated using dynamic light scattering measurements for further discussion.

\[
\begin{align*}
\text{Sample temperature (℃)} & \quad \text{MW×10}^9 \text{ (g/mol)} \\
10 & \quad 100 \\
1000 & \quad 20 30 40 50 60
\end{align*}
\]

\(\text{● with DBTL} \quad \text{〇 without DBTL}\)

### 3.2. Effect of Organic Solvents on the Mw of Micelle with Catalyst

In the DBTL-free aqueous solution (open circle in Figure 5), \(M_W\) increases linearly as the sample temperature increases. It is supposed that \(M_W\) increases according to the growth of the micelles. This can be attributed to enhanced hydrophobic interactions of surfactant molecules at higher temperatures, resulting in the growth of micelles. The \(M_W\) values of the aqueous solution with the addition of DBTL (closed circle in Figure 5) increase at all temperatures compared to the DBTL-free aqueous solution, leading to the assumption that DBTL is incorporated into the micelles. For the aqueous solution containing DBTL, the local maximum is observed in \(M_W\) at 40 ℃ as the temperature increases. The increase in \(M_W\) with increasing temperature up to the maximum value is thought to be due to stronger hydrophobic interactions of surfactant molecules and consequent micelle growth, as described above. On the other hand, the decrease in \(M_W\) with increasing temperature above the maximum value may indicate that DBTL is released, which is accompanied by shrinkage of the micelles [16].

The \(M_W\) (closed triangle) of the aqueous solution with DBTL and PrOH and the \(M_W\) (closed square) of the aqueous solution with DBTL and 2EhOH are shown in Figure 6, associated with data from Figure 5. As shown in Figure 6, by adding PrOH, \(M_W\) decreases slightly in the range of 25–40 ℃ and remained almost unchanged at 50 ℃. \(M_W\) reaches its local maximum at 40 ℃ similar to the case without PrOH. This can be explained by the fact that when PrOH is added, its incorporation into the micelles at 25–40 ℃ results in the partial release of DBTL instead. At 50 ℃, there is no change in \(M_W\) regardless of the presence of PrOH because a substantial amount of DBTL is released. When mixing 2EhOH, \(M_W\) is much lower at 25–40 ℃ than with PrOH. The plausible reason is that since 2EhOH is less soluble in water than PrOH, it is more easily incorporated into the micelles, so that a considerable amount of DBTL is released from the micelles.

![Figure 4](image_url)

**Figure 4.** Relationship between the curing speed constant (\(k\)) and curing temperature and the effects of the organic solvent on the curing behavior.

**Figure 5.** Relationship between the sample temperature and weight-average molecular weight (\(MW\))
3.2, the Mw of the micelles in the above samples will be slightly lower in the range of 25–40 °C and remained almost unchanged at 50 °C. Mw reaches its local maximum at 40 °C similar to the case without PrOH. This can be explained by the fact that when PrOH is added, its incorporation into the micelles at 25–40 °C results in the partial release of DBTL instead. At 50 °C, there is no change in Mw regardless of the presence of PrOH because a substantial amount of DBTL is released. When mixing DBTL-free aqueous solution, in which the mobility of DBTL molecules was presumably low. These differences are reflected in the above absolute temperature difference.

An absolute temperature difference was observed between the switch onset temperature (80 °C), as indicated by viscoelasticity measurements of the coating film and the results obtained in this study. In the former case, the results were obtained using a coating film with an extremely low water content, in which the mobility of DBTL molecules was assumed to be low. The latter case relates to an evaluation in an aqueous solution, in which the mobility of DBTL molecules was presumably high. These differences are reflected in the above absolute temperature difference.

3.3. Relationship between Characteristic Values of Organic Solvents and Switching Functionality

Regarding the organic solvents not mentioned above, k values were measured only at 70 °C (k70) and 100 °C (k100). Figure 7 shows k70 and k100 values for paint systems containing each organic solvent. Depending on the type of organic solvent, the k70 values vary remarkably, while k100 values remain almost unchanged. This indicates that when baking was performed at 100 °C, the blending of organic solvents had no influence on the...
The relationship between the characteristic values of organic solvents and k70/k100 values is discussed below.

Figure 7. The k70 and k100 values for paint samples with different solvent compositions.

Figure 8 shows the relationship between the water solubility of the organic solvent and k70/k100 values. Solvents with water solubility levels exceeding 10 g/100 mL are plotted as 20 g/100 mL in Figure 8 for convenience. As shown in Figure 8, no correlation between water solubility and the k70/k100 exists. Figure 9 shows the relationship between the boiling point of the organic solvent and k70/k100 values. The k70/k100 values increase with the increasing boiling point; in other words, the switchability decreases.

Figure 8. Relationship between water solubility at 20 °C and k70/k100 values.
3.4. Storage Stability of Paint

Figure 10 shows the increasing viscosity percentage levels of the paints containing each organic solvent. The percentages vary remarkably depending on the type of organic solvent. Here, the relationship between the characteristic values of the organic solvent and the increasing viscosity percentage levels is explained.

Figure 11 shows the relationship between the water solubility of the organic solvent and the increasing viscosity percentage levels. Solvents with water solubility levels exceeding 10 g/100 mL are plotted as 20 g/100 mL. As shown in Figure 10, no correlation can be found between the water solubility and the percentage of increasing viscosity. Figure 12 shows the relationship between the boiling point of the organic solvent and the increasing viscosity percentage levels.
viscosity percentage levels. Figure 12 shows that the increasing viscosity percentage levels increase with the increasing boiling point, which indicates that the storage stability tends to deteriorate.

![Figure 11](image1.png)

**Figure 11.** Relationship water solubility at 20 °C and increasing viscosity percentage levels.

![Figure 12](image2.png)

**Figure 12.** Relationship boiling point of the additional solvent and increasing viscosity percentage levels.

Next, the relationship between $k_{70}/k_{100}$ values and the percentage of increasing viscosity is shown and the characteristic values of organic solvents that have the ability for both switchability and storage stability are discussed.

3.5. **Switchability and Storage Stability**

Figure 13 shows a summarized relationship between the $k_{70}/k_{100}$ values and the increasing viscosity percentage levels. The $k_{70}/k_{100}$ value for standard paint without organic solvent was the lowest (gray plot in Figure 13), which increased after adding the organic solvent. This means that the switching functionality decreases with the addition of an organic solvent. However, for $k_{70}/k_{100} < 0.26$, the percentage of increasing viscosity after the storage stability test was almost the same and the storage stability in this range
was not a problem. On the other hand, for $k_{70}/k_{100} \geq 0.26$, the percentage of increasing viscosity increased monotonically with the increase of $k_{70}/k_{100}$ values. Next, the properties of organic solvents needed to achieve both switchability and storage stability are summarized regarding the water solubility and boiling point of the organic solvent.

Figure 13. Relationship between the $k_{70}/k_{100}$ of the additional solvent and the percentage of increasing viscosity.

Figure 14 shows the results for the percentage of increasing viscosity, which are highlighted by the water solubility and boiling point of the organic solvent. In Figure 14, the open circle plots represent the solvents for which the percentage of increasing viscosity was the same as without organic solvents (iPrOH, PrOH, BuOH, PrM, EtB), while the closed circle plots represent those for which the percentage of increasing viscosity was substantially higher than without organic solvents (2EhOH, Et2Eh). Solvents with water solubility levels exceeding 10 g/100 mL are plotted as 20 g/100 mL in Figure 13 for convenience. In Figure 14, it can be seen that if the water solubility is at least 10 g/100 mL and the boiling point is less than 200 °C, both switchability and storage stability can be achieved.

Figure 14. Water solubility at 20 °C and boiling point of the additional solvent allowing switchability and storage stability.
4. Conclusions

When 2-pack isocyanate waterborne paint (without organic solvents) encapsulating DBTL in nonionic surfactant micelles with hydrophilic–lipophilic balance of 13–14 in advance releases DBTL via the collapse of the micelles at 80 °C or higher, the curing progresses rapidly. On the other hand, the viscosity levels of the paint before and after being left at 40 °C for 1 h remain substantially unchanged. In this study, we investigated whether the above-described actual paint system containing organic solvents can develop a switching functionality in terms of maintaining storage stability at 40 °C and imparting a catalytic function for curing progress at 80 °C. Organic solvents with high hydrophilicity and low boiling points are less likely to be incorporated into the micelles and have less significant effects on the behavior of DBTL in the micelles, which in turn is less likely to be released. Further, it is also thought that a low boiling point for the organic solvent enhances volatilization upon heating, so that such solvents are less prone to being incorporated into the micelles. As a result, it was found that when the solubility of the organic solvent in water was at 20 °C is at least 10 g/100 mL and the boiling point was ≤ 200 °C, both curing and storage stability were achieved.

Author Contributions: Conceptualization, S.Y.; methodology, S.Y.; writing—original draft preparation, S.Y.; writing—review and editing, S.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable for this article.

Acknowledgments: The author would like to express their sincere gratitude to Hiroshi Nakamura of the Toyota Central R&D Labs, Inc., for their useful discussions and guidance in preparing this manuscript.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Bailey, M.E.; Kirss, V.; Spaunburgh, R.G. Reactivity of Organic Isocyanates. Ind. Eng. Chem. 1956, 48, 794. [CrossRef]
2. Wicks, D.A.; Wicks, Z.W., Jr. Blocked isocyanates III Part B: Uses and applications of blocked isocyanates. Prog. Org. Coat. 2001, 41, 1–83. [CrossRef]
3. Modi, S.; Spubler, A.; Jin, J. Impact of Automated, Connected, Electric, and Shared (ACES) Vehicles on Design, Materials, Manufacturing and Business Models; Center for Automotive Research: Ann Arbor, MI, USA, 2018.
4. Melchior, M.; Sonntag, M.; Kobusch, C.; Juergens, E. Recent developments in aqueous two-component polyurethane (2K-PUR) coatings. Prog. Org. Coat. 2020, 40, 99–109. [CrossRef]
5. Yomo, S.; Tachi, K.; Narita, T. Improving the appearance of 3-coat-l-bake multilayer films on automotive bodies. Prog. Org. Coat. 2018, 123, 299. [CrossRef]
6. Wicks, D.A.; Wicks, Z.W., Jr. Blocked isocyanates III: Part A. Mechanisms and chemistry. Prog. Org. Coat. 1999, 36, 148–172. [CrossRef]
7. Cram, D.J.; Cram, J.M. Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge, UK, 1994; Volume 4, p. 223.
8. June, Y.G.; Jung, K.I.; Choi, M.; Lee, T.H.; Noh, S.M.; Jung, H.W. Effect of Urethane Crosslinking by Blocked Isocyanates with Pyrazole-Based Blocking Agents on Rheological and Mechanical Performance of Clearcoats. Coatings 2020, 10, 961. [CrossRef]
9. Wang, L.; Zou, H.; Dong, Z.; Zhou, L.; Li, J.; Luo, Q.; Zhu, J.; Xu, J.; Liu, J. Temperature-Driven Switching of the Catalytic Activity of Artificial Glutathione Peroxidase by the Shape Transition between the Nanotubes and Vesicle-like Structures. Langmuir 2014, 30, 4013–4018. [CrossRef] [PubMed]
10. Kremer, C.; Schnakenburg, G.; Lutzen, A. Towards allosteric receptors—Synthesis of beta-cyclodextrin-functionalised 2,2’-bipyridines and their metal complexes. Beilstein. J. Org. Chem. 2014, 10, 814–824.
11. Zhu, X.; Xu, G.; Chamoreau, L.; Zhang, Y.; Mouries-Mansuy, V.; Fensterbank, L.; Bistri-Aslanoff, O.; Roland, S.; Sollogoub, M. Permethylated NHC-Capped Alpha- and Beta-Cyclodextrins (ICyDMe) Regioselective and Enantioselective Gold-Catalysis in Pure Water. Chem. Eur. J. 2020, 26, 15901–15909.
12. Quach, Q.; Biehler, E.; Elzamzami, A.; Huff, C.; Long, J.L.M.; Abdei-Fattah, T.M. Catalytic Activity of Beta-Cyclodextrin-Gold Nanoparticles Network in Hydrogen Evolution Reaction. *Catalysts* 2021, 11, 118. [CrossRef]

13. Ye, R.P.; Lin, L.; Liu, C.Q.; Chen, C.C.; Yao, Y.G. One-Pot Synthesis of Cyclodextrin-Doped Cu-SiO2 Catalysts for Efficient Hydrogenation of Dimethyl Oxalate to Ethylene Glycol. *Chemcatchem* 2017, 9, 4587–4597. [CrossRef]

14. Ikeda, A.; Shinkai, S. Novel cavity design using calix[n]arene skeletons: Toward molecular recognition and metal binding. *Chem. Rev.* 1997, 97, 1713–1734. [CrossRef] [PubMed]

15. Duchene, D. *New Trends in Cyclodextrins and Derivatives*; Edition de Sante: Paris, France, 1991; p. 449.

16. Yomo, S. Curing Behavior of Waterborne Paint Containing Catalyst Encapsulated in Micelle. *Coatings* 2021, 11, 375. [CrossRef]

17. Yomo, S.; Tachi, K. Improving appearance of 3-coat-1-bake multilayer films on automotive bodies through solvent composition design. *Prog. Org. Coat.* 2019, 137, 105318. [CrossRef]

18. Howard, P.H.; Meylan, W.M. *Handbook of Physical Properties of Organic Chemicals*; CRC Lewis Publishers: Boca Raton, FL, USA; New York, NY, USA; London, UK; Tokyo, Japan, 1997.

19. Mori, K. Method for Estimating Crosslink Density in Curing Process on Coating Films-Proportionality between Storage Modulus and Crosslink Density. *J. Jpn. Soc. Color Mater.* 2013, 86, 123. [CrossRef]

20. Zimm, B.H. The Scattering of Light and the Radial Distribution Function of High Polymer Solutions. *J. Chem. Phys.* 1948, 16, 1093–1099. [CrossRef]