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Synthesis of [9]-10-[9] Two-Directional Arborol for Adhesion Promoter in Polymer-on-Metal Composites

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Synthesis of one kind of cascade dendrimers which has hydroxy groups [9]-10-[9] two-directional arborol with dibromodecane core performed under two nucleophilic and amidation substitution reaction steps and its results were characterized by FT-IR and ^{13}C NMR. The produced dendrimer is suitable adhesion promoter in polymer-on-metal composites because this dendrimer has hydroxy groups and can make a link with some of polymers. They also have a good situation for surface absorbing on metal sheets. This dendrimer adhesion size were measured by mean of shearing strength tests and adhesion promoter process were studied in produced charts.

Key Words: Synthesis, Arborol, Polymer.

INTRODUCTION

Dendrimers are highly branched regular three-dimensional monodisperse macro-molecules with a branch occurring at each monomer unit[1]. Whereas linear polymers are built up from species with two reactive groups, dendrimers grow from repeated units that have three or more functionalities. Regular and repeated branching at each monomer group gives rise to a symmetric structure and pattern to the entire globular dendrimers. Many different kinds of multi-functional repeat groups can be used to synthesize the dendrimer, but they all shear the basic regions of core, branching layers and terminal groups[2] (Fig. 1).

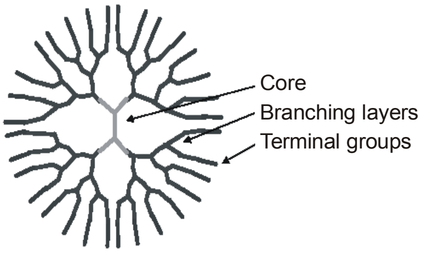

Fig. 1. Representation of dendrimer of third generation

Dendrimers are generally prepared either using a divergent method or a convergent one. In the divergent method dendrimers are built stepwise from a small polyfunctional core and through the reiteraction of a sequence of reactions. This sequence of reactions allows one to build dendrimers layer after layer and generation after generation[3]. But the convergent method consists of the branching of dendrons using the reactivity of their core. The convergent method suffers from steric constraints when the dendrons supposed to be linked to the core become too large[4,5].

Dendrimers are also known as starburst and cascade polymers. Since these cascade dendrimers are based on arboreal design, they are logically called arborols[6]. Sylvanols are thus the poly-pherical cascade analogues. The objective of this proposed research is to investigate the use of dendrimers as adhesion promoters for polymer-on-metal interfaces and to characterize the chemical and physical properties of the interface[7].

Arborols with hydroxy functional groups are to be used as adhesion promoters metal substrates are coated with arborol adhesion layer first and then the polymer layer is subsequently applied. Since arborols possess tens of functional groups at the end, the aggregate strength of these multidendate interactions with both the metal substrate and the polymer coating renders them a suitable choice for enhancing adhesions[8].

An arborol is dissolved in water when possible with a less than 3 wt % in concentration. The pre-cleaned metal plate is then dipped in to the arborol solvent solution for a certain period of time depending on the nature of the metal and the arborol. After removing the plate from the solution, it is then rinsed capiously with the solvent and dried in flowing nitrogen. The metal plate is now ready for further coating or characterization. Polymer is first dissolved in appropriate organic solvent and then simply applied on to the metal plate as thin film and then dried in vacuom. Polymers can be bonded to the metal surfaces by the proper choise of dendrimer promoters with desired functional groups, dendrimer with hydroxy end groups for example arborol can link with polyisocyanates to form urethane bonds[1,5,9-12].

In this paper, the synthesis and characterization of two-directional cascade molecules, [9]-10-[9] arborol, are reported. (The number [9] indicates the 9 hydroxy groups at two terminal and the number 10 is the number of carbons in the alkyl chains).

EXPERIMENTAL

Two directional arborol was prepared by a two step nucleophilic substitution and amidation procedure.

Step-I: 1,10-Dibromodecane (15 mmol) was added to a stirred solution of $NaC(CO_2Et)_3$ (34 mmol) in DMF (40 mmol) at 90 ºC. After 12 h, the solution was cooled and 100 mL toluene was added. This solution was washed with saturated (4 × 100 mL) $NaHCO_3$, dried over anhydrous $MgSO_4$ and remove the solvent by rotary.

Step-II: Ester (2 mmol) were synthesized and *tris*(hydroxymethyl)-aminomethane (12 mmol) were dissolved in 15 mL of Me_2SO_4 and stirred over anhydrous K_2CO_3 for 4-5 d at room temperature. The solvent was removed and finally the mixture was washed with water twice to get the arborol gel[5,13-17].

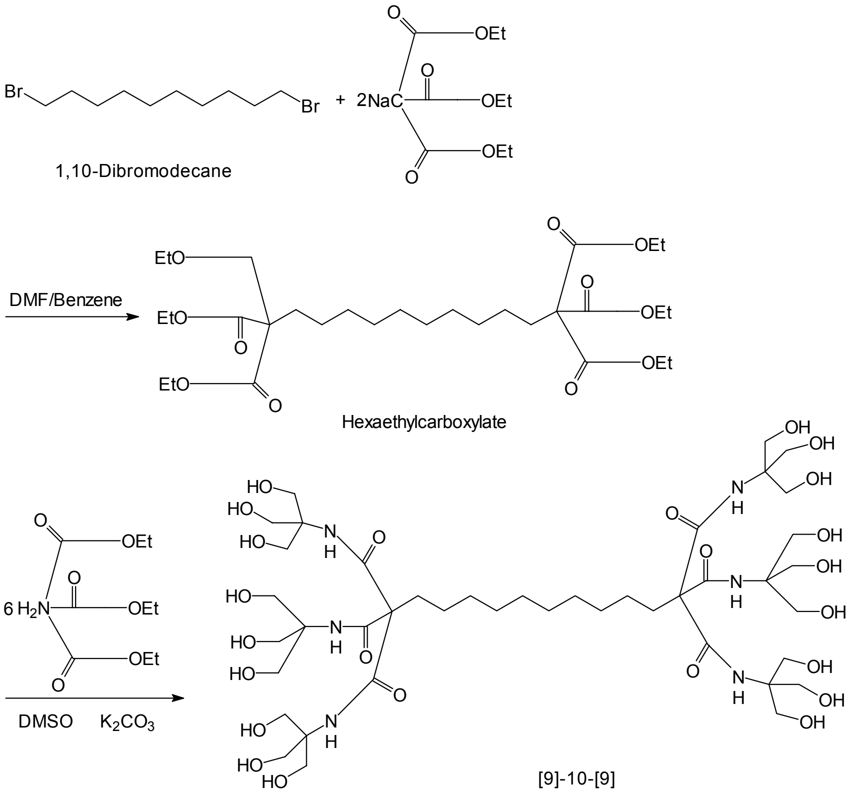

Fig. 2. Procedures to synthesize two directional [9]-10-[9] arborol

The mixture of epoxy resin and hardner was applied on the fabric piece using a steel sheet. To investigate the effect of arborol on adhesion quality of the studied composits, different arrangements for arborol addition were used. A reference composite was prepared with out any arborol surface treatment. Other composits were prepared with addition of different consistence of arborol[18,19].

Adhesion size of samples were measured by means of T-Peel test according to 3947 Iran standard. The accuracy of the results of strength tests of adhesive bonds will depend on the conditions under which the bonding process is carried out[1]. In order to ensure that complete information is available to the individual conducting the tests, the manufacturer of

TABLE-1
CATEGORIES OF SAMPLE CODES

Sample	Weight percent of epoxy	Weight percent of arborol
A1	100	0
A2	95	5
A3	75	25
A4	50	50

the adhesive shall furnish numerical values and other specific information for each of the following variables: (i) Procedure for preparation of the surfaces prior to application of the adhesive, the cleaning and drying of metal surfaces and special surface treatments such as sanding, wich are not specifically limited by the pertient test method. (ii) Complete mixing directions for the adhesive. (iii) Conditions for application of the adhesive, including the rate of spread or thickness of film, number of coats to be applied, whether to be applied to one or both surfaces and the conditions of drying where more than one coat is required. (iv) Assembly conditions before application of pressure, including the room temperature, length of time and whether open or closed assembly is to be used. (v) Conditioning procedure before testing, unless a standard procedure is specified, including the length of time, temperature and relative humidity[20].

RESULTS AND DISCUSSION

^{13}C NMR spectrum showd a resonance for each of the ten unique carbons. The successful transformation of ester to arborol is clearly evident upon comparison of their ^{13}C NMR spectra in that the C=O shifted downfield by 5 ppm [ester:167 ppm to arborol: 172 ppm] and the $-OCH_2CH_3$ resonances [ester: 62.2 and 14 ppm] were lost. The new peaks at 68 and 65.1 ppm were assigned to CNH and CH_2OH, respectively. Figs. 3 and 4 represent the ^{13}C NMR of ester and arborol, respectively.

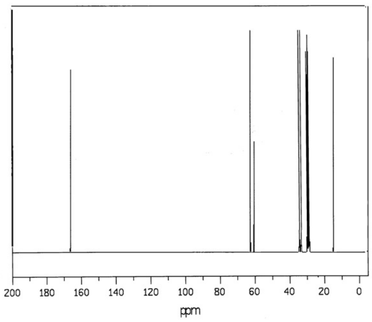

Fig. 3. ^{13}C NMR of hexaethyl carboxylate

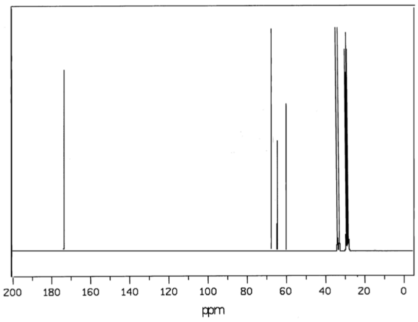

Fig. 4. ^{13}C NMR of [9[-10-[9] arborol

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