SYNTHESIS OF ISOTROPIC PITCH WITH HIGH SOLVENT SOLUBILITY USING HALOGEN

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Introduction

The petroleum-derived and coal tar-derived pitch materials are widely used as a precursor for high performance carbons such as carbon fiber [1], anode materials for Li-ion battery [2], and activated carbon materials [3]. Recently, carbon nanotubes [4], carbon nanofiber have been extensively studied as promising carbons. Electorospining [5] is well known to be able to prepare a new form of carbon nanofiber with diameter of hundreds nanometers. Nevertheless, the extensive studies have been carried out, pitches cannot be used as a precursor for the electrospinning because of its low solvent solubility and low molecular weight (<1000). In general, the electrospinning using pitch precursors with high softening point (over 250°C) have several problems to overcome as for the low molecular weight and low solvent solubility induced from the molecular structures. One of problems is to prepare a concentrated solution with high viscosity because pitch usually does not be soluble to solvent because of its high aromatic molecular structures. The other problem is to find the proper solvent with proper boiling point which is able to produce solidified spun pitch fiber around room temperature [6].

In this study, the present authors have tried to prepare novel synthetic pitches which have a high molecular weight and a high solvent solubility through the dehydrogenation of 2-methylnaphthalene (2MN) to connect 2MN with flexible alkyl chains by adding halogen materials at relatively low temperature. The bromination using 2MN will be expected to afford a unique structure of obtained isotropic pitches with alkyl-bridged connections for the requirement property of both high solvent solubility and high molecular weight. The authors have investigated the structures, characteristics and synthetic mechanism of produced pitch. Additionally, we applied obtained pitch to produced carbon fiber and eletrospun carbon nanofiber by melt and Electrospinning, respectively.

Experimental

Preparation of isotropic pitch

2MN (purity>96.0) and bromine (Br_2, JIS Special Grade) were used in this study without further purification. The preparation of 2MN-derived isotropic pitch was carried out in a 500 ml Pyrex flask with the agitation system of 150 rpm under N_2 atmosphere. The bromination of 2MN was carried out at various temperatures from 30°C to 210°C. After reaching to the desired temperature, Br_2 was dropped to add to reactor with the rate of 50 ml/h, and after Br2 adding, further heat treatment was carried out with vigorous stirring for another 30 min. After reaction, the brominated material was cooled down to room temperature.

The continuous heat treatment of the brominated material was carried out with stirring of 200 rpm under N_2 flow of 200 ml/min at 320°C with a heating rate of 2°C/min. The reaction for polymerizing and condensing was done at 320°C for 6 h, 12 h and 24 h, respectively. Table 1 summarized the preparation conditions of pitches.

Table 1. Preparation conditions and some properties of obtained pitches

Sample name	Amount of Br_2 (mole ratio)	Bromination temp.	HTT		Yield	S.P.	Mw	solubility			
		°C	°C	hr	wt%	°C		n-hexane	toluene	THF	pyridine
2MN_1.0	1.0	180	320	6	45	93	435	80.0	100.0	100.0	100.0
				12	32	95	421	76.8	97.0	100.0	100.0
				24	15	90	491	61.2	91.9	100.0	100.0
2MN_1.5	1.5			6	48	104	523	60.4	97.8	100.0	100.0
				12	38	112	552	60.0	97.2	100.0	100.0
				24	22	113	480	52.1	83.8	100.0	100.0
2MN_2.0	2.0			6	51	153	797	27.6	94.4	99.8	100.0
				12	42	168	799	24.5	89.0	97.6	100.0
				24	40	183	823	20.8	81.1	96.8	100.0

n-Hexane (JIS Special Grade) was used as a solvent for removal of light weight molecules of produced pitches. Cut off fractions of pitches were used as precursors for melt spinning and Electrospinning.

Characterization of isotropic pitch

The brominated and heat-treated products were characterized with ^{1}H-NMR and ^{13}C-NMR in a solvent ($CDCl_3$), using tetramethylesilane as an internal standard. The softening points (S.P.) of the isotropic pitches were measured by using thermo mechanical analyzer (TMA).

Molecular weight and its distribution of pitches were measured with Laser Desorption/Ionization Time of Flight Mass Spectroscopy (LDI TOF-MS). The solvent solubility of the pitch was evaluated by solvent extraction method.

Results and Discussion

Influence of bromination temperature

The brominated products of 2-MN at 30°C and 180°C were investigated by ^{1}H-NMR analysis as shown in Figure 1. 1-bromo-2-methylnaphthalene as a main product was synthesized by the bromination at 30°C. On the other hand, 2-(bromo) methylnaphthalene (2BMN) was mainly synthesized by bromination at 180°C. The bromination temperature made the difference of dehydrogenation point. In our study, the bromination of 2-MN was adopted at 180°C because of the effective introduction of methylene connections of 2-MN molecules for obtaining the flexible structures of prepared isotropic pitch.

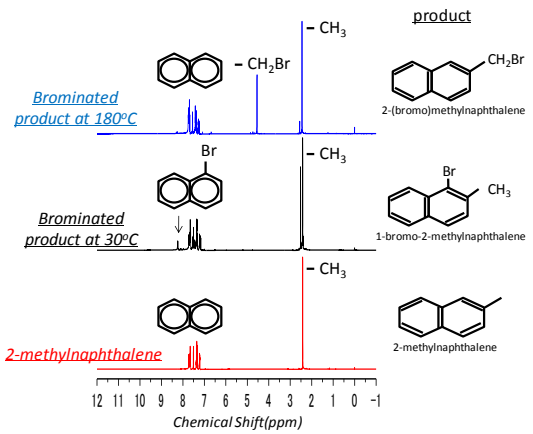

Fig. 1 ^{1}H NMR spectra of 2-methylnaphthalene and brominated-products at 30°C and 180°C

Reaction of isotropic pitch

The synthetic mechanism of isotropic pitch through the bromination and continuous heat treatment was schematically expressed in Figure 2. Figure 3 shows the molecular weight distribution which is determined by TOF-MS. In the Fig. 3, we know the very regular polymerization occurred in the after heat treatment of the brominated products, confirming the methylene bridged connections of 2-(bromo) methyl-naphthalene each others.

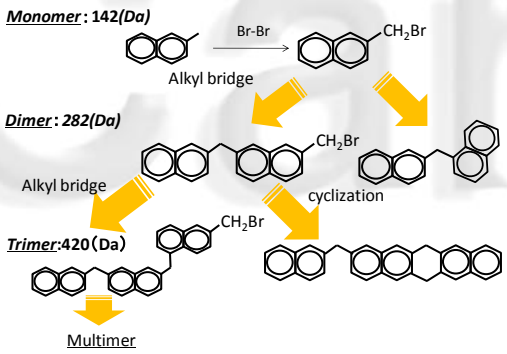

Fig. 2 Schematic synthetic mechanism of isotropic pitch

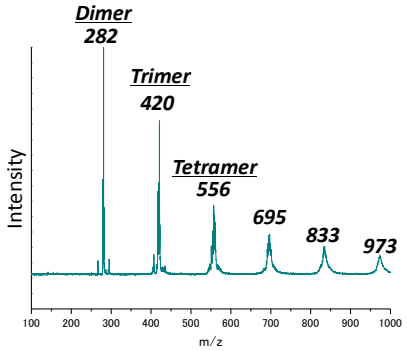

Fig. 3 Molecular weight distribution of synthesized pitch by TOF-Mass

Some properties of pitches after the hexane-cut were summarized in Table 2. The high softening point of pitch over 250°C with over 1500 of averaged molecular weight (Mw) can be successfully achieved by the series of processes of the bromination, after heat treatment and hexane cut-off of light molecules.

Table 2. Some properties of pitch with *n*-hexane cutoff

Sample name	Amount of Br_2 (mole ratio)	HTT hr	S.P. ℃	Mn	Mw	PDI (Mw/Mn)
2MN_1.0_HI	1.0	6	208	632	743	1.17
		12	222	785	941	1.20
		24	219	713	913	1.28
2MN_1.5_HI	1.5	6	228	948	1256	1.32
		12	235	961	1400	1.46
		24	252	1142	1600	1.40
2MN_2.0_HI	2.0	6	212	1038	1482	1.43
		12	217	1154	1593	1.38
		24	249	1223	1694	1.38

Electrospinning of isotropic pitch

The prepared pitches with high molecular weight were successfully electrospun. Details of the pitch-based carbon nanofibers will be shown in the presentation of conference.

Conclusions

The pitches having high solvent solubility, high molecular weight and high softening point were successfully synthesized the series of processes of the bromination, after heat treatment and hexane cut-off of light molecules of 2-MN. The obtained pitch can be used for the effective precursors for melt and electrospinning to obtain carbon fiber and carbon nanofibers, respectively.

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References

[1]I. Mochida. Mesophase pitches prepared from methyl naphthalene by the aid of HF/BF_3, CARBON 1991; 29: 561-567
[2]A. Mabuchi. Charge-discharge characteristics of the mesocarbon microbeads heattreated at different temperatures, Journal of the Electrochemical Society 1995; 142(2): 1041-1046
[3] M. Suzuki. Activated carbon-fiber - fundamentals and applications, CARBON 1994; 32(4): 577-586
[4] S. Iijima. Helical microtubules of graphitic carbon. Nature 1991;354:56–8
[5] M,Bognitzki. Nanostructured fibers via electrospinning. ADVANCED MATERIALS 2001; 13(1):70-
[6] S. H. Park. Preparation of pitch-based CF/ACF web by electrospinnig, CARBON 2003; 41:2653-2689