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REACTIONS WITH SAMARIUM DIIODIDE IN POLYMER SYNTHESIS

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Abstract: Reactions induced by SmI_2, such as reduction, coupling and cyclization are occurring in high yield upon mild conditions. It is due to the high redox potential of divalent samarium. Now reactions with SmI_2 are used in the polymer synthesis as well. By the coupling reaction of various diacid chlorides poly-α-diketones having molecular weight up to 20000 have been obtained at room temperature in quantitative yield. Isomeric difluorobenzils prepared by the one-step reaction of SmI_2 and relevant fluorobenzoyl chlorides have been used in the nucleophylic substitution reaction with bisphenols. Film-forming high molecular weight copolyetherketone-α-diketones have been synthesized when such difluorobenzils have been used as the comonomers in the polycondensation of 4,4'-difluorobenzophenone and bisphenols. All these polymers bearing α-diketogroups have been transformed into linear and network polyquinoxalines by their reaction with aromatic (bis)o-diamines. Aromatic polypinacols have been synthesized by the reaction of dialdehydes and SmI_2 in THF under mild conditions. The availability of the reactive α-hydroxy groups made it possible to carry out polymer chain reactions. It was stated that the imide cycle is reduced by SmI_2 at room temperature. The treatment of polyimides by SmI_2 leads to the change of polymer properties, mainly heat resistance and solubility. The possibility of formation of Si-Si bonds by reductive coupling of organochlorosilanes with the use of SmI_2 instead of Na has been shown. It was found that the reaction of diorganodichlorosilanes with SmI_2 easily proceeds in THF solution at room temperature to yield α,ω-dichloro-oligosilanes.

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Recently much attention has been paid to the application of lanthanide elements in organic chemistry. Among such elements divalent samarium reagents, mainly SmI_2, are widely used as reaction coreagents or initiators for effective performing of reduction, cyclization, coupling and many other organic reactions (Ref. 1). It is due to high redox potential of Sm(II) (-1.55 V) and the solubility of cited Sm(II) derivatives in certain organic solvents. The mild conditions, namely, room temperature and short reactions times, are the main advantages of such processes. Therefore the attempt of the divalent samarium derivatives application in polymer chemistry is assumed to be very attractive. It is especially promising to use the reactions which proceed selectively in high, better quantitative, yield. The application of such reactions for the more simple formulation of known and novel monomers is interesting as well. Finally, the study of novel reactions with usage of divalent samarium for the polymer synthesis and modification process is undoubtedly an important problem. Therefore this paper consists of three main parts, namely,

- the synthesis of polymers by the reactions with SmI_2, known in organic chemistry;
- the synthesis of monomers by the reactions with SmI_2 the their application in polymer forming reactions;
- the study of novel reactions based on the usage of SmI_2 for the polymer synthesis and reactions.

The results of our studies as well as results of other authors investigations are used.

SmI_2 is smoothly produced by the reaction of metallic samarium with diiodomethane or 1,2-diiodoethane in oxygen-free dried THF (Ref.2).

$$Sm + ICH_2\text{-}CH_2I \longrightarrow SmI_2$$

There are a few cases where this reagent has been directly prepared in other solvents, namely, tetrahydropyran, acetonitrile, pivalonitrile (Refs. 3-6). As it was stated recently, organic reactions mediated by SmI_2 are slower in pivalonitrile than in THF, but selectivities are often improved, reactions being greatly accelerated by addition of catalytic amounts of some transition metal salts, for example, iron acetylacetonate or nickel halides (Ref.6).

Besides SmI_2 bis-cyclopentadienylsamarium, bis-pentamethylcyclopentadienyl samarium and $SmBr_2$ are used (Refs. 7-9). The preparation of the latter is based on the reduction of tribromosamarium (easily available from Sm_2O_3) by a lithium dispersion (Ref. 9). Such approach allows preparations on a large scale.

The rather unusual condensation reaction of SmI_2 and acid chloride giving α-diketone in high yield under mild conditions was chosen as an approach to polymer formation:

$$\text{XCORCOX} + SmI_2 \longrightarrow \text{-[-CO-R-CO-]}_n\text{-}$$

where R = m(p)-C_6H_4, p-C_6H_4-R'-C_6H_4-p'; R' = -O-, -$C(CF_3)_2$- , etc.

X = Cl, F.

We synthesized α-diketone homo- and copolymers in a quantitative yield by the reaction of cited diacid chlorides or -fluorides with SmI_2 in THF at room temperature for 10-15 min (Refs. 10-11). The influence of acid chloride - SmI_2 molar ratio , the order of reagents introduction and reaction time on the chemical structure of resulting polymers has been studied. When diacid chloride is added to SmI_2 solution, polymers having both α-diketone and α-hydroxyketone groups are obtained. The reverse order of reagents adding and an increase in their concentration lead to the rise in the α-diketone groups content and polymer molecular weight.

The polymers obtained have amorphous structure, molecular weight up to 25000 and Tg of 250-290°C. These polymers are readily soluble in various organic solvents. The treatment of poly-α-diketones by aromatic o-di- and tetramines leads to the formation of linear and network polyquinoxalines having improved heat resistance in comparison with their precursors.

The coupling reaction of acid chlorides under influence of SmI_2 has been used for the preparing of some bifunctional monomers, namely, isomeric difluorobenzils. The latters have been obtained by the condensation under mild conditions of p-and o-fluoro-benzoyl chlorides and SmI_2 in THF.

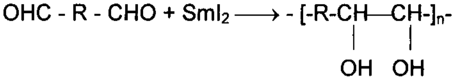
A paraffin-like admixture of C_{23-25} alkanes was also detected in the unpurified reaction product. These alkanes can be produced as a result of the oligomerization of ethylene, formed at an early step in the reaction of metallic samarium with diiodoethane. SmI_2 or

SmI_2Cl might serve as the oligomerization initiator both in the SmI_2 formation reaction and the subsequent α-diketone synthesis.

These activated difluoroaromatic compounds have been used for the synthesis of high molecular weight aromatic polyether-α-diketones by the nucleophylic substitution of fluorine atom by alkali metal phenoxides. Relevant high molecular film-forming copolymers have been synthesized by the polycondensation of difluorobenzils, 4,4'-difluorobenzophenone and bisphenols and transformed in polymers having quinoxaline moieties.

Another approach to the application of Sm^{+2} promoted reactions in polymer chemistry is based on the synthesis of pinacols from aldehydes. The treatment of various aldehydes, especially (un)substituted benzaldehyde, by SmI_2 gives hydroxybenzoins in high (up to 95%) yield (Ref. 1). When dialdehydes are used as substrates in such reaction it is possible to obtain polypinacols which are promising as reactive polymers. It is known that previously only low molecular weight oligomers having diol structures have been prepared by reductive coupling of terephthalic dialdehyde by chromium (III) sulphate/zinc redox pair or titanium (IV) chloride/ zinc (Refs. 12,13).

By treating dialdehydes with SmI_2 we firstly synthesized polypinacols having molecular weight about 12-15 × 10^3 (Ref.14):



$$OHC-R-CHO + SmI_2 \longrightarrow -[-R-\underset{OH}{CH}-\underset{OH}{CH}-]_n-$$

R = p (m)C_6H_4, etc.

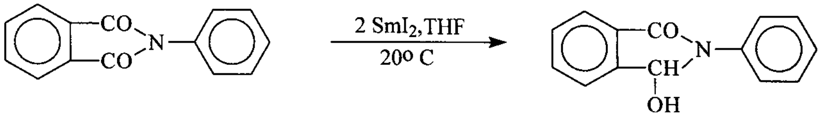
Then Wege and Greiner (Ref. 15) have obtained similar OH-functionalized poly(p-xylylenes) by a similar procedure. They have stated that oligomers synthesized (M_n = 4-5 × 10^3) are soluble in NMP, DMF, DMSO, benzyl alcohol, and also in a mixture of THF (acetone, methanol, and ethanol) and water. No signifcant side reaction was detected in model reactions under optimal reaction conditions. The low molecular weight of polymers is probably due to the precipitation of the product while polyreaction advances.

The synthesis of polyoxamides is the next example of polymer forming reactions based on the application of SmI_2. It was shown (Ref. 16) that coupling reaction of isocyanates promoted by SmI_2 takes place:

$$\mathrm{RNCO} \xrightarrow[2)\ \mathrm{H_3O^+}]{1)\mathrm{SmI_2/HMPA}} \mathrm{R-NH-CO-CO-NH-R}$$

The reaction of different diisocyanates, namely, 4,4'-diisocyanatodiphenyl methane, 2,6-toluene diisocyanate, 4,4'-diisocyanato-3,3'-dimethyldiphenyl methane, 2,6-di-isocyanato naphthalene with SmI_2 in THF under catalytic influence of HMPA at -30 - 67°C leads to polyoxamides in almost quantitative yield, insoluble in organic solvents (Ref. 17). The successful introduction of alkyl groups into oxamide moieties of polymers provided not only highly soluble N-alkylated polymers (M_n up to 9000) but also an opportunity for further polymer modification.

Above Sm^{+2} promoted polymer forming reactions based on relevant organic reactions known have been discussed. Now we will consider the reaction of SmI_2 with polyimide as a substrate (Refs. 18, 19). The tendency of imides to transformations under the influence of SmI_2 was initially estimated on the model reaction of N-phenylphthalimide. Upon adding of the latter to a mixture of SmI_2 with Sm (2 : 1) at room temperature the colour of reaction mixture was quickly changed from blue-green to cherry-violet, indicating a change in valence state of Sm. Based on ^1H NMR and IR spectroscopic data and chemical analysis results the reduction of one of imide CO groups was fixed:



According to the same analytical methods such cyclic imide remains significantly unchanged at a stoichiometric ratio of SmI_2 and imide. When the excess of SmI_2 increases, more profound changes occur due to the further reduction of CHOH group under the influence of SmI_2, with N-phenylphthalimidine formation.

It is interesting that the SmI_2 treatment of N-acetylcaprolactam, having both a cyclic and an acyclic CO group, gives a product having two reacted CO groups, one of them, namely, cyclic one is reduced to CH_2 group whereas the other (in acetyl moiety) is reduced to CHOH group. (In contrast to imides lactams are stable under similar conditions.)

The reaction of polyimide with SmI_2 leads to the formation of network polymer having reduced imide cycles. Probably the curing of polymer is due to intermolecular reactions of the resulting OH groups.

The final part of this paper is devoted to the usage of SmI_2 for the synthesis of polysilanes which have specific physical, mainly optical, properties. The common method of polysilanes synthesis is based on the Wurtz-Fittig reaction of organodichlorosilanes and alkali metals. This approach has a set of disadvantages, namely, rigorous reaction parameters, low process selectivity, and the difficulty in preparing reactive polysilanes having tailored molecular weight characteristics (Ref. 20). The recent methods are rather complex, comprise many steps and are characterized by low yields of the target products (Ref. 21).

It was shown (Ref. 22) that the application of Sm^{+2} permits to advance a one-step method for the synthesis of hexaorganodisilanes from triorganochlorosilanes:

$$2\,R^1R^2R^3\,SiCl \;+\; 2\,SmI_2 \longrightarrow (R^1R^2R^3Si)_2 \;+\; 2\,SmI_2Cl$$

Radicals	Yield, %
$R^1 = R^2 = R^3 = Me$	< 5
$R^1 = R^2 = Me$, $R^3 = Vinyl$	75
$R^1 = R^2 = Me$, $R^3 = Ph$	85
$R^1 = R^2 = R^3 = Ph$	90

It was stated that, as with common organic compounds, the mode and rate of the reaction and the yield of target product depend on the organochlorosilane used. Benzyl and allyl substituted chlorosilanes dimerize most effectively.

It was also shown (Ref. 23) that the reaction of diorganodichlorosilanes with SmI_2 affords oligosilanes. On the other hand, by the cocondensation of dichlorosilanes with monochlorosilanes under influence of SmI_2 linear and cyclic oligosilanes are formed. The use of SmI_2 instead of alkaline metal has a set of advantages, namely, the reaction may be carried out homogeneously in THF medium at lower temperature (66°C instead 144°C) for a shorter time.

Thus the reactions mediated by two-valent samarium derivatives open novel interesting possibilities for the formulation of polymers and their subsequent modification. Further studies are necessary for preparing more high molecular weight polymers, the decrease of Sm amount and its utilization.

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REFERENCES

(1) N. E. Brandukova, Ya. S. Vygodskii, S. V. Vinogradova, *Russian Chem. Revs.* **63**, 345 (1994)
(2) J. L. Namy, P. Girard, H. B. Kagan, *New J.Chem.* **1**, 5 (1977)
(3) J. L. Namy, M. Colomb, H. B. Kagan. *Tetrahedron Lett.* **35**, 1723 (1994)
(4) M. Murakami, M. Hayashi, Y. Ito. *Applied Organometal. Chem.* **9**, 385 (1995)
(5) J. Inanaga, M. Ishikava, M. Yamaguchi. *Chem Lett.* 1485 (1987)
(6) B. Hamann, J. L. Namy, H. B. Kagan. *Tetrahedron*, **45,** 14225 (1996)
(7) J. L. Namy, J. Collin, J. Zhang, H.B.Kagan. *J.Organometal. Chem.* **328**, 81 (1987)
(8) W. J. Evans, G. Kociok-Kohn, V. S. Leong, W. J. Ziller. *Inorg. Chem.* **31**, 3592 (1992)
(9) A. Lebrun, E. Rantze, J. L. Namy, H. B. Kagan. *New J.Chem.* **19**, 699 (1995)
(10) V. V. Korshak, S. V. Vinogradova, Ya. S. Vygodskii, N. A. Churochkina, N. E. Brandukova. *Vysokomol. Soedin.*, A **29**, 1480 (1987)
(11) N. E. Brandukova, Ya. S. Vygodskii, T. V. Strelkova. *Vysokomol. Soedin.* A **38**, 1803 (1996)
(12) J. M. Hoyt, K. Koch. *U.S. Patent* 3 509 097 (1970)
(13) A. W. Cooke, K. B. Wagenar. *Synth. Met.* **29**, E525 (1989)

(14) N. E. Brandukova, Ya. S. Vygodskii, S. V. Vinogradova. *Vysokomol. Soedin.* A **36**, 10 (1994)

(15) V. U. Wege, A. Greiner. *Acta Polymer.* **46**, 391 (1995)

(16) Y. S. Liu, M. Z. Bei, Z. H. Zhou, Y. Fujiwara. *Chem. Lett.* 1143 (1992)

(17) J. Wang, R. Nomura, T. Endo. *J. Polymer Sci., Polymer Chem.* **33**, 2901 (1995)

(18) N. E. Brandukova, Ya. S. Vygodskii, L. I. Komarova, T. V. Strelkova. *Russian Chem. Bulletin.* **45**, 1176 (1996)

(19) N. E. Brandukova, Ya. S. Vygodskii, L. I. Komarova, T. V. Strelkova. *Vysokomol. Soedin.*, B **38**, 2045 (1996)

(20) R. D. Miller, J. Michl. *Chem. Rev.* **89**, 1359 (1989)

(21) J. Chusciel, E. Fossum, K. Matyjaszewski. *Polymer Preprints.* **34**,221 (1993)

(22) B. G. Zavin, A. I. Chernyavskii, Ya. S. Vygodskii, N. E. Brandukova. *Dokl.Akad Nauk*, **336**, 365 (1994) [*Dokl.Chem.*, **336**, 97 (1994) (Engl. Transl.)]

(23) O. A. Petukhova, A. I. Chernyavskii, B. G. Zavin, N. E. Brandukova, Ya. A. Vygodskii. *Russian Chem. Bulletin*, **45**, 1449 (1996)