

## Benefits of Using IEM in Various Applications

### Abstract

2-Isocyanatoethyl methacrylate<sup>1</sup> (CAS# 30674-80-7), also known as IEM, is a multifunctional compound with versatile practicality in a variety of applications. This technical whitepaper highlights two representative use cases of IEM as a value-added differentiator in mission-critical applications, namely as a coupling agent to compounds containing active hydrogen groups and as used in polymerization reactions.

### Background

IEM is a clear liquid with a hue ranging from colorless to slightly yellow. Its melting and boiling points are -45 °C and 211 °C, respectively<sup>1</sup>. Regarding its solubility, IEM is miscible in aprotic solvents such as acetone and toluene<sup>2</sup>.

Structurally, as may be seen in Figure 1, IEM is a bifunctional compound containing an isocyanate (blue) and a methacrylate group (red).

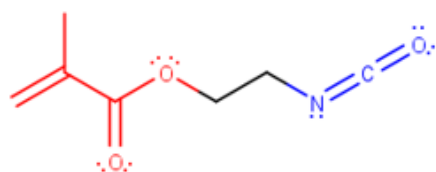


Figure 1. Structure of IEM.

The isocyanate contains an electrophilic carbon (flanked by the more electronegative oxygen and nitrogen), which is accordingly subject to ready attack by a nucleophilic center bonded to an active hydrogen (e.g., the oxygen of a different compound's hydroxy group) so as to primarily form an anion on the nitrogen<sup>3,4</sup>. The active hydrogen (AH, as it will now be denoted) is then bonded with the negatively charged nitrogen to form an IEM-capped derivative with, when the AH group of the aforementioned "different compound" (DC) is an alcohol or amine, a water-resistant urethane or urea linkage, respectively. In addition to water, such derivatives—which include "blocked" IEM compounds derived from single-AH-containing but hindered groups such as  $\epsilon$ -caprolactam or MEKO—can then successfully mingle with other AH-containing compounds that IEM might otherwise react with, including protic solvents such as ethanol<sup>2</sup>. If the DC contains multiple AH groups, the polymerizable vinyl C=C double bond of IEM's methacrylate group may likewise be introduced at each site. This IEM-capped derivative would then be able to participate in later crosslinking polymerizations, inducible upon the introduction of heat and/or ultraviolet light into the reaction chamber<sup>2</sup>. The present initiator would subsequently undergo homolytic scission to form the free radicals<sup>5</sup>.

Alternatively, IEM (or blocked-IEM) may be polymerized first to form a linear polymer with pendant (or pendant and blocked) isocyanate functionality incorporated along the polymer backbone. If this chain polymer were then mixed with, e.g., a linear step or chain polymer containing terminal or pendant alcohol functionality, the two functionalities may react to form urethane-containing branches or crosslinks. The blocked isocyanates would de-block at case-specific elevated temperatures before reacting<sup>2</sup>. Reaction of either isocyanate form with a linear step or chain polymer would thus result in branched or network polymers, respectively<sup>5</sup>. As such, IEM hosts two groups with crosslinking capabilities, and formation of a rigid thermosetting plastic occurs when the network polymer is of sufficiently high crosslink density<sup>5</sup>.

While IEM may be less reactive than certain aromatic isocyanates (e.g., toluene diisocyanate) due to its lesser electron delocalization, as an aliphatic isocyanate IEM is more UV-stable and less susceptible to thermally-induced degradation<sup>6</sup>. These characteristics happen to align nicely with IEM's use in such environments for polymerization and crosslinking. Thus, compared to aromatic isocyanates, IEM would perform better in applications demanding color stability<sup>6</sup>. Compared to acrylates (e.g., 2-acryloyloxyethyl

<sup>1</sup> Another widely used name is methacryloyloxyethyl isocyanate.

isocyanate), polymers with methacrylate functionality tend to have improved impact resistance (e.g., in automotive coatings) and exhibit better weathering<sup>7</sup>. Lastly, IEM's isocyanate and methacrylate group react as one might predict from similar groups in other compounds<sup>2</sup>. For instance, the vinyl reactivity of IEM is similar to methyl methacrylate (MMA)<sup>2</sup>. Ultimately, IEM is a versatile monomer across a range of applications, and two usage groupings are briefly presented below.

## Representative Cases of IEM as a Value-added Differentiator

### Usage 1: IEM as a Coupling Agent to Compounds Containing Active Hydrogen Groups

A review of the patent literature reveals IEM's extensive use in the capping of alcohol-containing compounds, which may be carried out neat or in aprotic solvents (e.g., DCM, toluene)<sup>8</sup>. When used, solvents should be moisture-free (i.e., "dry"); the reactivity of water with isocyanate is similar to primary alcohols, and higher than more sterically-hindered alcohols<sup>2,4</sup>. Even the presence of trace water may result in the conversion of IEM molecule isocyanates to primary aliphatic amines, which more rapidly react with the isocyanates of other IEM molecules to yield disubstituted ureas<sup>2,4</sup>. Indeed, the reactivity of IEM with compounds containing such amines is such that a catalyst is not required for the reaction to rapidly proceed to high yield even at 25 °C<sup>9,10</sup>. Reaction temperatures for the coupling of IEM to alcohol-containing compounds range from 25–80 °C, with yield generally increasing alongside temperature<sup>2,11,12</sup>. Catalysts such as the organotin DBTL or tertiary amine DABCO may be employed, with their use becoming especially necessary at room temperature (i.e., as temperature is decreased) due to the accompanying lower sensitivity of IEM's isocyanate to alcohols<sup>2,13</sup>. IEM may be protected against premature or unwanted polymerization by adding an inhibitor (e.g., BHT) and carrying out capping reactions under an oxygen atmosphere<sup>5</sup>. Autoxidation of unsaturated monomers by oxygen frequently leads to the generation of peroxidic compounds capable of generating radicals at relatively low temperatures and thus initiating polymerization, which the inhibitor is added to suppress<sup>14</sup>.

As already alluded to, IEM may cap sterically-hindered monofunctional compounds with just one *AH* group to form blocked derivatives of IEM (e.g., IEM-caprolactam, IEM-MEKO). Such IEM derivatives dissociate at elevated "de-blocking" temperatures, the exact value determined by the blocking group used but within the approximate range of 70–200 °C, to regenerate the free isocyanate of IEM<sup>15</sup>. As will be further discussed in the following usage section, formulations may be designed that polymerize at a lower temperature than the system temperature employed to regenerate the isocyanate, which would then readily react with an *AH* group.

One illustrative example of where IEM may be explored as a coupling agent to alcohol-containing compounds is the synthesis of, from various copolymers, pendant-ethylenic-group-containing prepolymers used as ingredients in UV-curable formulations cast-moldable into contact lenses<sup>16</sup>. Also, IEM has prepared UV-curable dimethacrylate-functionalized perfluoropolyether crosslinking monomers (from PFPE diol) for elastomeric dielectric films used in organic field effect transistors (OFETs)<sup>17</sup>. Lastly, terpolymers with pendant methacrylate functionality were added as ingredients to coating solutions sprayed onto medical devices (e.g., coronary stents) and subsequently thermally crosslinked to form polymeric network layers thereon<sup>18</sup>.

### Usage 2: IEM in Polymerization Reactions

Free-radical copolymerization of IEM (or blocked-IEM) with different vinyl monomers, as well as homopolymerization, may be carried out neat or in dry aprotic solvent; i.e., via bulk or solution polymerization<sup>2,5</sup>. When used, a solvent that dissolves initiator, monomer(s), and also the polymer to be synthesized should be chosen; e.g., toluene for the AIBN-initiated generation of poly(IEM-*co*-MMA)<sup>5,9</sup>. Beside the azo initiator AIBN, a peroxide initiator may be selected when thermal polymerization is desired<sup>5</sup>. While 25–100 °C may be acceptable, 50–80 °C is a more ideal window for both effecting initiator homolysis in thermal polymerization and lowering the potential for "runaway" exothermic reaction<sup>19,5</sup>. Higher

temperatures also increasingly favor side reactions such as chain transfer and branching<sup>14</sup>. For UV-induced “photopolymerization”, photochemical initiators (e.g., benzoin methyl ether) that decompose more efficiently upon exposure to the radiation are better used<sup>5</sup>. Reaction times, typically ranging from 10 minutes to 24 hours, are influenced by the amount of initiator present in addition to reaction temperature<sup>20,21,14</sup>. Timescales for heat-induced curing (e.g., to form hardened coatings) have been on the bottom end of this range, while crosslinking of UV-curable formulations may complete south of 25 seconds<sup>18,12,16</sup>. One might presume such outcomes would partly stem from the much shorter crosslinks created during curing, in contrast to, e.g., the synthesis of long-chain (high-molecular-weight) linear polymers from monomer units. In contrast to this whitepaper’s first usage section, radical polymerizations should generally be carried out under an inert atmosphere (e.g., nitrogen, argon)<sup>5,22</sup>. Oxygen should be excluded in order to remove any possibility of introducing weak peroxide polymer backbone links, via peroxy radicals otherwise formed during initiation, which lead to premature polymer degradation during processing at high temperatures<sup>5</sup>. RAFT polymerization may be seen as a bridge of sorts between the groupings of free-radical and reversible-deactivation (“living”) polymerization, with the latter producing better-defined polymers with narrower dispersity through suppression of the termination mechanism<sup>5</sup>. Essentially a free-radical polymerization but with an added chain transfer agent (e.g., a dithiobenzoate), RAFT polymerization was utilized in an AIBN-initiated reaction to yield poly(IEM-co-MMA) with low dispersity (i.e.,  $\bar{M}_w/\bar{M}_n = 1.23$ ). The copolymer was then crosslinked with a diamine to form nanoparticles of controlled size and pre-determined arrangement of functional groups for application in such fields as microelectronics and drug delivery<sup>9,23,24</sup>.

For applications involving blocked-IEM, a blocking agent with dissociation temperature safely above that employed for polymerization should be selected<sup>25</sup>. Liberated blocking agent could otherwise act as a chain-transfer agent, leading to products with broader molecular weight distribution and even the formation of low-molecular-weight oligomers from premature termination<sup>25</sup>. Otherwise, designing a system that takes advantage of a blocked isocyanate monomer’s ability to safely polymerize in the presence of polyfunctional *AH*-containing compounds, with such a system “self-curing” upon heating to the de-blocking temperature, conveniently allows for the preparation of one-component (1K) coatings<sup>25,26</sup>. As with blocking reactions, de-blocking reactions may be accelerated by the use of certain catalysts (e.g., DBTL)<sup>2</sup>. IEM-MEKO has found use in the preparation of 1K urethane coatings because MEKO is a liquid with boiling point (152 °C) near the system’s de-blocking temperature<sup>25</sup>. Accordingly, MEKO acts as a solvent while also volatilizing out of, instead of remaining in, the coating<sup>25</sup>. Finally, in contrast to suspension polymerization, initiators used in emulsion polymerization, which happen to typically be persulfates or redox systems, must be soluble in the aqueous dispersion medium—which is usually water in either case<sup>5</sup>. Due to the isocyanate being masked, blocked-IEM monomers may be safely polymerized in both processes.

There have been numerous uses of IEM’s polymerization capabilities in different industry applications. Photoalignment coating copolymer solutions, synthesized from IEM comonomer, demonstrated improved adhesion to optical substrates when UV-cured<sup>27</sup>. Additionally, copolymer emulsions derived from pyrazole-blocked IEM comonomer were used to prepare water/oil repellent agents with good adhesion as coatings for fiber products (e.g., sportswear), electronics, concrete building materials, etc.<sup>28</sup>. Lastly, polymerized latex particulates with improved color and water stability for inkjet printing formulations were prepared from MMA and a phenol-blocked IEM comonomer<sup>15</sup>. Upon dispersion of particulate in water and later de-blocking of the isocyanate, the resultant amine became covalently tethered to the latex<sup>15</sup>.

## **Varsal Advantage**

Varsal is a leading producer of extremely-high-purity IEM. We are differentiated from the competition as Varsal’s proprietary manufacturing logistics processes allows us to produce consistent,

stable, extremely-high-purity material—leading to maximal yield and product quality for Varsal’s customers.

Extremely high purity in monomers such as IEM is important because of the sheer diversity of obtainable products from different polymerization systems, with a variety of reaction kinetics<sup>29</sup>. Even trace impurities can significantly affect product quality and lead to poor reproducibility of desired compounds<sup>29</sup>. This may be seen, for instance, in the case of living anionic polymerization, which has been widely used to produce well-defined block copolymers with blocks of controlled stereochemistry, predefined molar mass, and narrow molar mass distribution<sup>5</sup>. However, the high reactivity and low concentration of the carbanionic active centers result in the high susceptibility of anionic polymerization to inhibition by even trace impurity quantities<sup>5</sup>. The living end-groups must be retained throughout the reaction in order to form block copolymers (e.g., from styrene and IEM), so the use of extremely-high-purity monomers is imperative<sup>5</sup>.

Varsal is able to serve a wide variety of end-markets and applications, as our intimate knowledge of the manufacturing process allows us to custom-manufacture various grades of IEM tailored to our customers’ requirements. Please contact us at [info@varsal.com](mailto:info@varsal.com) to learn more about how Varsal can help you solve your complex chemical and specialty intermediates challenges!

<sup>1</sup> Literature, from public SDS information.

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<sup>7</sup> “Comparison of Performance of Acrylate and Methacrylate Aliphatic Urethanes.” 2004. M. deLombard-Watts and P. Weissman.

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